Synthesis of Oligo(Vinyl Ether)s in *ab initio* Cationic Polymerisation

By Weihong Lang

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Certificate of Originality

This is to certify that I am responsible for the work submitted in this thesis, that the original work is my own except as specified in acknowledgments or in footnotes, and that neither the thesis nor the original work contained therein have been submitted to this or any other institution for a higher degree.

(Signed) Weihong Lang

(Date) 15/6/2002

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Abstract

Terminally functionalised oligo(vinyl ether)s were produced in ab *initio* cationic polymerisations. Various polymerisations and chain end functionalisation systems were investigated. MALDI-TOF mass spectrometry was applied to analyse the obtained oligomers and thus the polymerisation and chain end functionalisation process.

Oligo(isobutyl vinyl ether), also oligo(ethyl vinyl ether) and oligo(methyl vinyl ether) were synthesised in cationic polymerisation. Silyl enol ethers were added to the polymerisation as end-capping agents before initiations and they compete with monomer to cap the carbocationic chain end. The methodology relies on a comparable end capping rate to chain propagation rate so that oligomers can still be produced in the presence of reactive end-capping agents whilst other side reactions are suppressed.

Polymerisation temperatures investigated range from -78°C to the room temperature (21°C), 4 out of 6 silyl enol ethers were applied and are proved to be reactive in the end-capping. Initiation systems investigated include iBVE-HCl/$Yb(OTf)_3$ and iBVE-HCl/$SnCl_4$ and both produced oligomers with high chain end functionalities. Generally silyl enol ether functionalised oligo(vinyl ether)s have lower molecular weights and broader molecular weight distributions than their identical control polymerisations without end-capping. The iBVE-HCl/$SnCl_4$ initiation system produced functionalised oligomers with narrower molecular weight distribution than iBVE-HCl/$Yb(OTf)_3$ initiation system.

Different silyl enol ether reactivities in end-capping were observed. It was also observed that *ab initio* chain end functionalisation by reactive silyl enol ethers largely suppressed the majority of side reactions during polymerisation. This suppression was attributed to the higher rates of end-capping than side reaction rates.

When (1-*tert*-butyl-vinyloxy)trimethyl-silane was applied as end-capping agent, the polymerisation system produced oligomers with narrower molecular weight distributions than the control polymerisations without end-capping while the chain end functionalities were also obtained. This indicates the possibility of setting up a controlled *ab initio* chain end functionalisation cationic polymerisation system in which the oligomer's molecular weight, polydispersity and chain end functionality can be regulated at the same time.

MALDI-TOF MS, NMR and SEC are mainly applied in the oligomer characterisation. Side reactions in this polymerisation system were examined from these analyses. Under less critical polymerisation conditions 7 different chain ends from side reactions are observed in MALDI-TOF mass spectra. Based on the MS and NMR observation the various chain end structures are identified. Side reactions are also postulated which mainly include β-proton elimination, water capping of the carbocationic chain end and combinations of these.

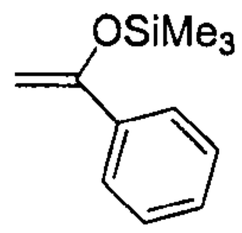
Sample preparation for MALDI-TOF MS analysis of oligo(vinyl ether)s is investigated. Direct laser desorption of oligo(isobutyl vinyl ether) was observed for the samples of molecular weight of up to 2k Daltons. Complementary information of oligo(isobutyl vinyl ether)s obtained from ESI MS indicates a serious mass discrimination in MALDI-TOF MS technique and thus it is regarded that MALDI-TOF MS can not provide reliable molecular weight distributions for polymers with broad molecular weight distributions.

Combination of SEC and MALDI-TOF MS to calibrate SEC columns and quantitative application of MALDI-TOF MS to analyse the oligomers' chain end functionalities were also explored.

Abbreviations

ACTH:	Adrenocorticotropic Hormone
AgTFA:	Silver Trifluoroacetate
CTMS:	Chlorotrimethylsilane
DBMP	2,6-di-*tert*-butyl-4-methylpyridine
DCM:	Dichloromethane
DHB:	2,5-Dihydroxy Benzoic Acid
DMF:	N, N-dimethylformamide
ESI MS:	Electrospray Ionisation Mass Spectrometry
EVE:	Ethyl Vinyl Ether
iBVE:	iso-Butyl Vinyl Ether
IR:	Infrared
LCST:	Low Critical Solution Temperature
LS:	Light Scattering
MALDI-TOF MS:	Matrix Assisted Laser Desorption/Ionisation- Time of Flight Mass Spectrometry
MWD:	Molecular Weight Distribution
M_n:	Number Average Molecular Weight
M_w:	Weight Average Molecular Weight
MAP:	4-Methoxy Acetonphonone
MVE:	Methyl Vinyl Ether
NMR:	Nuclear Magnetic Resonance
ODVE:	Octadecyl Vinyl Ether
OEVE:	Oligo(Ethyl Vinyl Ether)
OiBVE:	Oligo(isobutyl Vinyl Ether)
OMVE:	Oligo(Methyl Vinyl Ether)
PMMA:	Poly(Methyl Methacrylate)
PD:	Polydispersity
PIB:	Polyisobutene
SEC:	Size Exclusion Chromatography
SEE:	Silyl Enol Ether
TEA:	Triethylamine
THF:	Tetrahydrofuran

SEE 1



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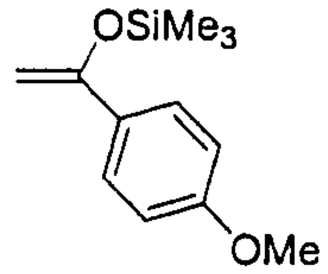

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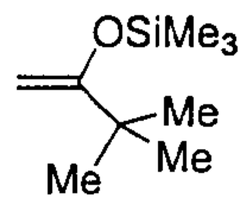

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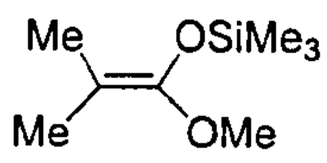

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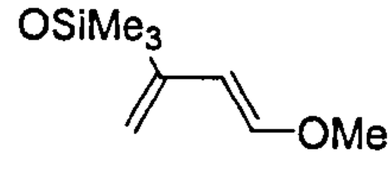

(3-Methoxy-1-methylene-allyloxy)-trimethyl-silane

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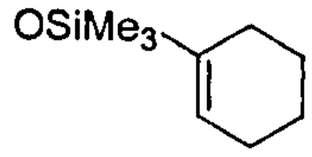


(Cyclohex-1-enyloxy)-trimethyl-silane

Contents

Chapter 1. Introduction

A polymer is a collection of macromolecules that are composed of repeat units joined through chemical bonds. Polymers can be classified into synthetic polymers and natural polymers. Natural polymers like proteins, nucleic acid and cellulose etc. usually have more complicated structures than synthetic polymers. Synthetic polymers generally have simpler and smaller repeat units. Various aspects of the structure of synthetic polymers are usually investigated in a sequence of synthesis, characterisation, behaviour and application.

Synthetic polymers were originally known as 'organic colloids' during the nineteenth century. It was the scientists' continuous exploration that finally concluded that these 'organic colloids' were actually true organic macromolecules, and a large variety of applications of polymers have been made since their discovery. Synthetic polymers like plastics, fibers, elastomers, coatings and adhesives etc., are closely related to our day-to-day life.

Since the1960s synthetic macromolecules have been increasingly recognized as organic reactants which behave like small organic species. Merrifield et al. firstly used polymers as reactive molecules in organic synthesis using the 'solid-phase technique' in 1963 [Merrifield, 1963]. New types of functionalised polymeric materials have been developed recently. Functional polymers are macromolecules with attached chemically functional groups that provide reversible or irreversible physical or chemical reactivities. The functional polymer can be synthesised by chemical modifications of pendant groups attached either to synthetic organic polymers or to naturally occurring polymers such as polysaccharides or inorganic supports. The applications of functional polymers are developing rapidly with great potential. They have been applied as stoichiometric reagents, catalysts, substrate carriers in organic syntheses and separations, biologically active agents, conductive materials, and photoresistant materials etc.

The development of new polymer materials with specific properties requires a high degree of control over the synthesis technique as well as design of new monomers and the functionalisations of the polymers. The difference between polymers and their small organic molecule counterparts lies in the polymer's bulk

structures and their special physical properties. By controlling the structures and functionalities of the designed polymers specific properties can be obtained.

1.1 Telechelic oligomers

Oligomers are short-chain polymers; the name originates from the Greek word. *oligo*, meaning few, and *mer* meaning part [Ebdon, 1991]. The different concept between polymer and oligomer is based on the bulk physical and mechanical properties which significantly depend on chain length. Very often this dependent phenomenon appears when the repeat unit is between 10 to 100 when the entanglement between chains happened.

Oligomers can be made by a variety of polymerisation processes and the reactive end-groups can be introduced during the oligomerisation or in a second stage and can be designed or suitably modified for the specific type of polymerisation.

There have been increased interests in oligomers with terminal functional groups since the 1980s. Typical end groups include hydroxyl, thiol, halide, carboxyl, amine, and acrylate, etc.. Developments in this methodology have allowed further reactions of the oligomers in the synthesis of block copolymers, graft copolymers and polymeric networks, which are difficult to obtain through conventional polymerisation techniques.

When end-groups are bifunctional, then the oligomers behave as *macromonomers*. The term *macromonomer* was coined by Milkovich in 1974 [Danzig, 1977; Milkovich, 1972] to describe some of the oligomers of styrene prepared by anionic polymerisation and having terminal vinyl groups capable of addition polymerisation. Today it is applied to cover any oligomers having at least one homopolymerisable or copolymerisable end group. In summary, *macromonomers* are polymerisable oligomers. They are ideal intermediates in the synthesis of well-defined branched, comb, graft and block copolymers. Generally macromonomers have functionalised chain ends like vinyl, styryl, methacroyl, epoxy etc.. Kennedy and Frisch reported the synthesis of polyisobutylene with a styryl α-end in 1980 and 1982, which can be used to synthesis branched polyisobutylene, graft or block copolymer. However, sterically hindered 1,2-disubstituted alkenes do not readily homopolymerise. In an earlier study, Sawamoto and co-workers [Sawamoto, 1986] synthesised functionalised polyisobutyl vinyl ether, in which a vinyl ether ω-end is

produced through end-capping of living polymerisation with sodium salt of di-ethyl-2-vinyloxyethylmalonate ($Na^+C^-(COOEt)_2CH_2CH_2OCH=CH_2$).

When the oligomers' end-groups are behaving as monofunctional groups, the oligomers are termed *telechelic oligomers*. The term *telechelic* was firstly proposed by Uraneck et al. in 1960 [Uraneck, 1960] to describe the linear polymers possessing two reactive terminal functions. It is again from Greek. *tele* means far or distant, *chelos* means claw. Goethals broadened this term to monotelechelic, ditelechelic and tritelechelic polymers.

Telechelics cause great interest from both academic research and industry. In academic research, for example, telechelic oligomers are used to synthesis special model networks in which crosslinked elements are equal in length. This model construct is important for network research and the theory of rubber elasticity.

Telechelics are quite often liquids due to their low molecular weight. They therefore have a relatively low viscosity and can be used at relatively low temperatures to prevent possible degradation. As there is no necessity to melt the thermoplastic this saves energy and with their well-defined chain-end functionalities they can be readily converted into high molecular weight polymers. The extension or crosslinking reactions of telechelic oligomers give end-products which show little shrinkage, this is a desirable characteristic, especially for moulding applications. Commercially available telechelics include hydroxy-terminated polytetrahydrofuran, polybutadienes and siloxanes.

Oligomers with ionic terminal groups are ionomers. The ionic groups can be aggregates both in solid and in solution. Aggregation in solid state leads to crosslinking. Because aggregation in solution leads to high solution viscosties, ionomers show potential as viscosity modifiers. Also, oligomers can be used as modifiers in thermosetting resins and in thermoplastics, as viscosity modifiers, plasticisers and emulsifiers.

Where applicable, it is advantageous to prepare the oligomers by a polymerisation mechanism offering the greatest control over initiation, propagation and termination steps. Living cationic, anionic and group transfer polymerisations offered the best control over the polymerisation systems.

1.2 Cationic polymerisation

1.2.1 Cationic polymerisation in general

Polymerisation is a process that links monomers into a polymer. The process is mainly divided into step-growth polymerisation and chain-growth polymerisation.

Step-growth polymerisation is applied for monomers with functional groups such as hydroxyl, carboxyl and acid chloride etc. and is often a succession of condensation reactions during which small molecules are eliminated and thus monomers are linked together.

The chain-growth polymerisations for olefinic monomers are chain reactions which convert the monomers into polymers by stimulating the opening of the double bond with a free radical or ionic initiator. According to the different growing species the chain-growth polymerisation mainly contains radical polymerisation, anionic polymerisation and cationic polymerisation. Among the three major types of chain polymerisation, cationic and anionic polymerisations belong to ionic polymerisation in which the growing species carry positive or negative charge. When the growing species carry positive charges during the process of chain growth, the polymerisation belongs to cationic polymerisation. Both alkenes and heterocyclic monomers can be polymerised cationically.

1.2.2 History of the development of cationic polymerisation

The scientific foundations of cationic polymerisation were laid by Friedel and Crafts around 1877. They found that $AlCl_3$ and other similar metal halides induced a large variety of chemical transformations, including alkylations and acylations. They attested their first carbocationic polymerisation by their publication on the polycondensation of benzyl chloride by $AlCl_3$ [Cowie, 1991].

The initial remarkable cationic research was performed by the team of Thomas-Sparks [Thomas, 1940] in the late 1930s at Esso, followed by P. J. Flory at the same company. Their research led to high molecular weight polyisobutylenes, butyl rubbers and halobutyl rubbers. Little scientific progress was made in the following 20 years.

In 1956 Szwarc started 'living' anionic polymerisation [Szwarc, 1956a; Szwarc, 1956b] and the research on anionic polymerisation thrived in the mid 1960s.

Well-defined narrow molecular weight distribution polystyrenes, various multiblock copolymers and thermoplastic elastomers have been developed using new methodologies since then. During the same period investigations in carbocationic polymerisation were mainly phenomenological. Synthetic chemists could not control the polymer's molecular weight, molecular weight distribution and chain end functionality in cationic polymerisation. In the mid 80s alkyllithium mediated anionic polymerisation reached its maturity while new carbocationic polymerisation techniques slowly came to prominence.

In the 1970s Kennedy et al. put effort into obtaining controlled cationic initiation and termination [Kennedy, 1976; Kennedy, 1977a], synthesis of well-defined block and graft copolymer [Kennedy, 1975a; Kennedy, 1975b; Vidal, 1976; Kennedy, 1977b; Vidal, 1977; Vidal, 1980] and controlled chain transfer [Kennedy, 1983]. Also sterically hindered bases were applied in cationic polymerisation for molecular weight and molecular weight distribution control [Kennedy, 1979]. Not until the 1980s did the processes of quasiliving, living or controlled cationic polymerisation appear [Faust, 1988; Kennedy, 1987; Miyamoto, 1984; Sawamoto, 1982b; Higashimura, 1979].

The drive in carbocationic techniques is toward 'macromolecular engineering', which means the synthesis of well-defined polymers with designed structures. The design of initiation systems, chain end functionalisation systems, chain transfer systems and monomers etc. can give polymers, copolymers and polymeric networks with desired molecular weight, molecular weight distribution and special physical properties. Not only the conventional materials such as rubbers, plastics, thermoplastic elastomers, blending agents, adhesives and sealants etc., were prepared by cationic polymerisations, but also the well-defined specialty products, including specialties for biomedical applications like artificial organs, drug delivery systems, and microelectronic applications and water purification membranes.

Although cationic polymerisation is limited to the synthesis of low molecular weight polymers, it is the preferred route when the electrophilic end groups need to be involved which are sensitive to nucleophilic attack. Cationic polymerisation of cyclic siloxanes with Si-H bonds is the only possible route due to the cleavage of Si-H bonds by nucleophiles.

Many commercial products have been produced cationically so far, including polyacetal, poly(tetramethylene glycol), poly(ε-caprolactam, polyaziridine, polysiloxanes, butyl rubber, poly(N-vinyl carbazol), polyindenes and poly(vinyl ether)s. Cationic polymerisation is also an attractive laboratory technique used to prepare specialty polymers with desired properties, especially the recent living cationic polymerisation techniques to prepare polymers and copolymers with controlled molecular weights and polydispersities. It is expected that living systems which produce block-copolymers and functionalised polymers will be commercialized in the near future.

1.2.3 Cationic polymerisation mechanism

Most cationic polymerisations are chain polymerisations involving positively charged or electrophilic active centres at the growing chain end. In addition, there is also step growth cationic polymerisation processes which involve oxidative coupling and Friedel-Crafts reactions during chain propagation.

Chain growth cationic polymerisation

The mechanism of chain growth cationic polymerisation can be defined by comparing the reactions of alkene monomers and heterocyclic monomers.

Both alkenes and heterocyclic monomers can be polymerised cationically. Cationic polymerisation of alkene monomers proceeds via the opening of the double bond while ring-opening polymerisation proceeds via the opening of the ring. Both of the polymerisations take place by nucleophilic attack at the electrophilic active centre. Very often the nucleophile in a vinyl monomer cationic polymerisation is a double bond and in ring-opening polymerisation it becomes the electro-rich heteroatom. Both the polymerisations include chain initiation, propagation and termination procedures and both polymerisation processes are sensitive to solvent and counterion.

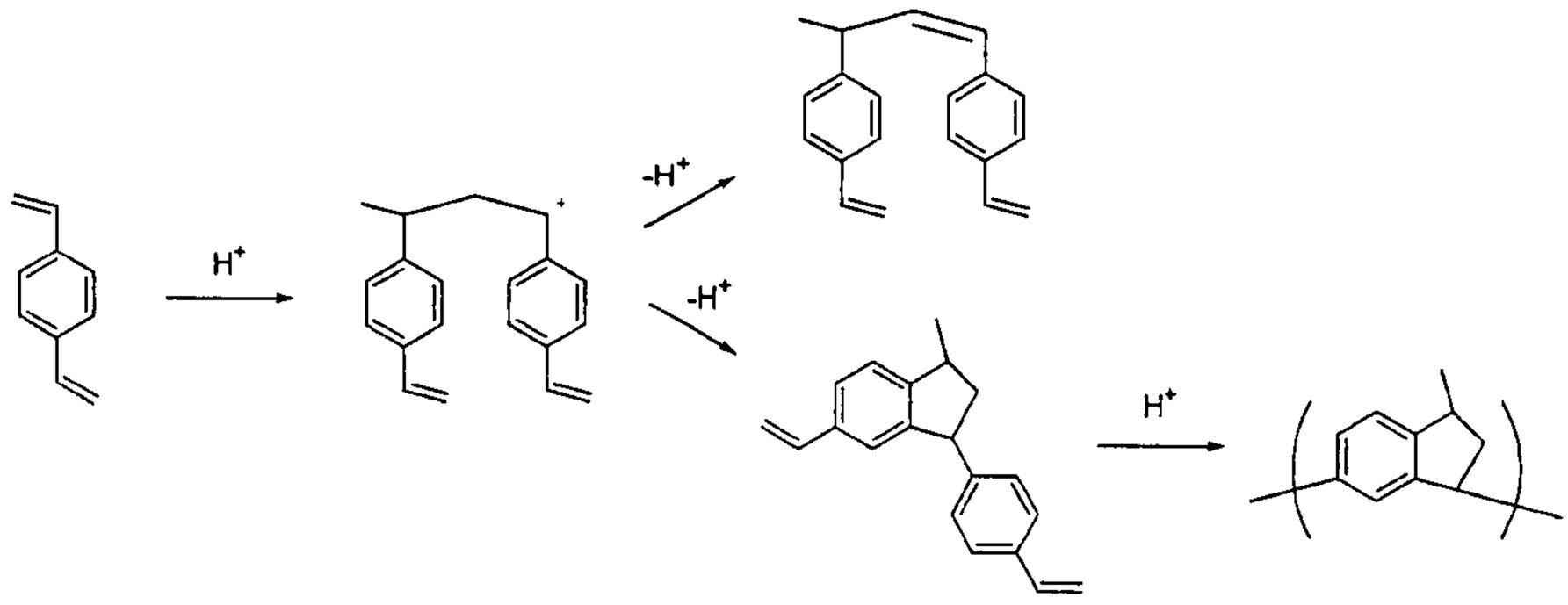
Because both cationic polymerisations of vinyl monomers and ring-opening polymerisation of heterocyclics proceed on electron-deficient active species based on the same cationic mechanism, basic principles hold for both vinyl and ring-opening cationic polymerisations. However, the main difference between them [Matyjaszewski, 1996b] is that polymerisation of vinyl monomers produces polymers with all-carbon backbone, but the ring-opening polymerisation produces the heteroatom incorporated backbones. Polymers prepared by ring-opening

polymerisation could have various sequences of carbon atoms and heteroatoms on the backbone. The two polymerisations have different types of active species, with the cationation of vinyl monomers giving a carbenium ion, and the cationation of heterocyclic monomers resulting in an onium ion. Living cationic ring-opening polymerisation conditions can be approached because of the low reactivity of the onium ion.

The heteroatoms contained in the polymer backbone are sufficiently nucleophilic to participate in the reaction so that chain transfer to the polymer is often observed in ring-opening polymerisation. The all-carbon backbone from a vinyl-monomer cationic polymerisation becomes the neutral component. Generally the vinyl-monomer cationic polymerisation is an irreversible reaction but ring-opening polymerisation of moderate to large ring is highly reversible.

Step-growth cationic polymerisation

Although step-growth electrophilic oligomerisation and polymerisation reactions have not been investigated as much as chain-growth electrophilic polymerisations, they can be used in the synthesis of oligomers and polymers which can not be obtained be alternative routes [Percec, 1997]. Benzylic carbenium ions were the first type of propagating species to be investigated, whilst other types of propagating species include: positively charged sulfur atoms, acylium cations, phenoxenium ions, cation radicals and zwitterions. A typical polymerisation of 1,4-divinylbenzene to give a linear poly(vinylbenzene) is described in the following scheme 1-1.



Scheme 1-1: Step-growth cationic polymerisation of 1,4-divinylbenzene

Protonation of the vinyl groups gives a carbenium ion followed by dimerisation with the vinyl group of a second molecule. The dimer can either undergo a β-elimination reaction giving the α,β-unsaturated group, or undergo an internal Friedel-Crafts alkylation reaction, followed by deprotonation to give the indane structure. Repeat reactions alternatively give a poly(vinylbenzene) with unsaturated groups in the main chain, or polyindanes.

1.2.4 Cationic polymerisation process

The research in the thesis relates to chain-growth cationic polymerisation of alkenes. An understanding of the cationic polymerisation mechanism requires a discussion of the mechanisms of fundamental reactions of initiation, propagation, transfer, termination and other reactions. Similar with free radical polymerisation, ionic polymerisation processes include chain initiation, propagation, transfer and termination.

Initiation means the initial formation of active species carrying a free radical, positive or negative charge. Initiation processes in cationic polymerisation include ion generation and cationation processes which give the active species that is able to add to monomer. Repeat electrophilic addition of the active species to monomer forms the polymer chain. Unlike free-radical polymerisation, the ionic polymerisations never terminate by combination or by disproportionation. Instead the termination is due to the irreversible deactivation of growing species, including unimolecular reactions or chain transfer to reactive terminating reagents, such as the reactions with nucleophiles in the system, formation of inactive covalent species and formation of unreactive carbenium ions.

Chain initiation

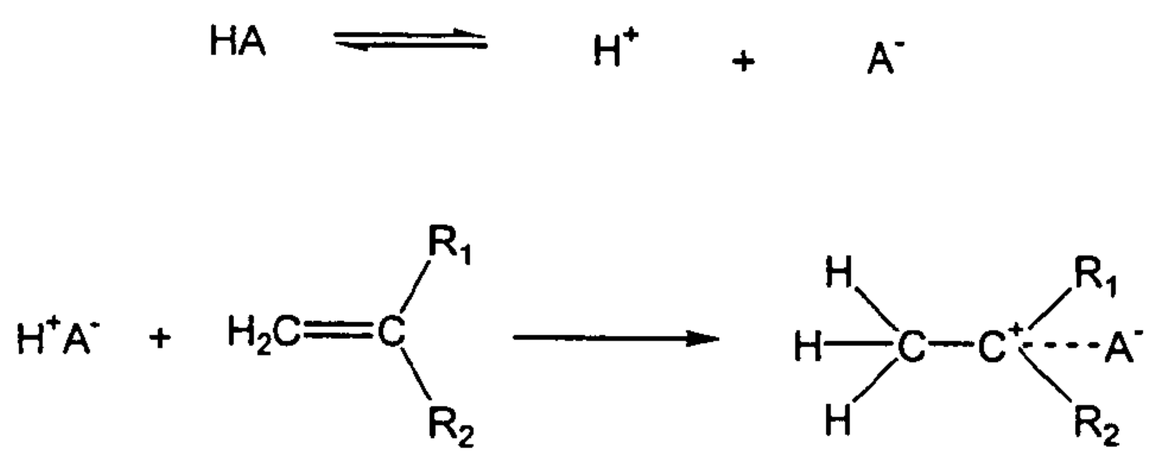
The initiation process is important in controlling molecular weight and its distribution, and also the topology of a polymer. The relative rates of initiation and propagation, i.e., the initiation efficiency, affect the molecular weight distribution of the polymer. Complex initiating systems consisting of a protonation agent and a Lewis acid have been developed to control both the overall rate of polymerisation and the molecular weight distribution. The structure of the initiator can provide a site for side reactions. When it contains a stable functional group this can facilitate the formation of macromonomers and telechelics. This has been used extensively in vinyl

ether polymerisations. Functional groups are also capable of reacting with the active species and thus need to be protected. When a multi-initiation site is involved in an initiator, star-shaped polymers can be prepared, for example, a new hexafunctional initiator [Cloutet, 1998] was applied in the cationic polymerisation of styrene to form a hexa-arm polystyrene.

Ideal initiators should be stable at room temperature and should generate the growing species quantitatively. The growing species should also remain active throughout the entire polymerisation. During cationic polymerisation the active centre of the growing chain can be either unpaired cations or cations that are paired and associated closely with counterions. The active species can be prepared by many different chemical and physical methods. Chemical methods include reaction with protonic acids [Pielichowski, 1973; Tsuda, 1960], Lewis acids, stable carbon cations, certain metal alkyls and direct oxidation of radicals etc. Physical methods include photochemically generated cations [Hua, 2001; Crivello, 1996; Bolln, 1996] and high-energy irradiation.

Usually initiators for ionic polymerisation are specific for certain monomers. Initiators for alkene cationic polymerisation include protonic acids, Lewis acids, stable carbenium ions, oxidizing reagents and other strong electrophiles [Matyjaszewski, 1996].

The protonic acid initiated cationic polymerisation depends upon the nucleophilicity of the conjugate base. The scheme is shown below.



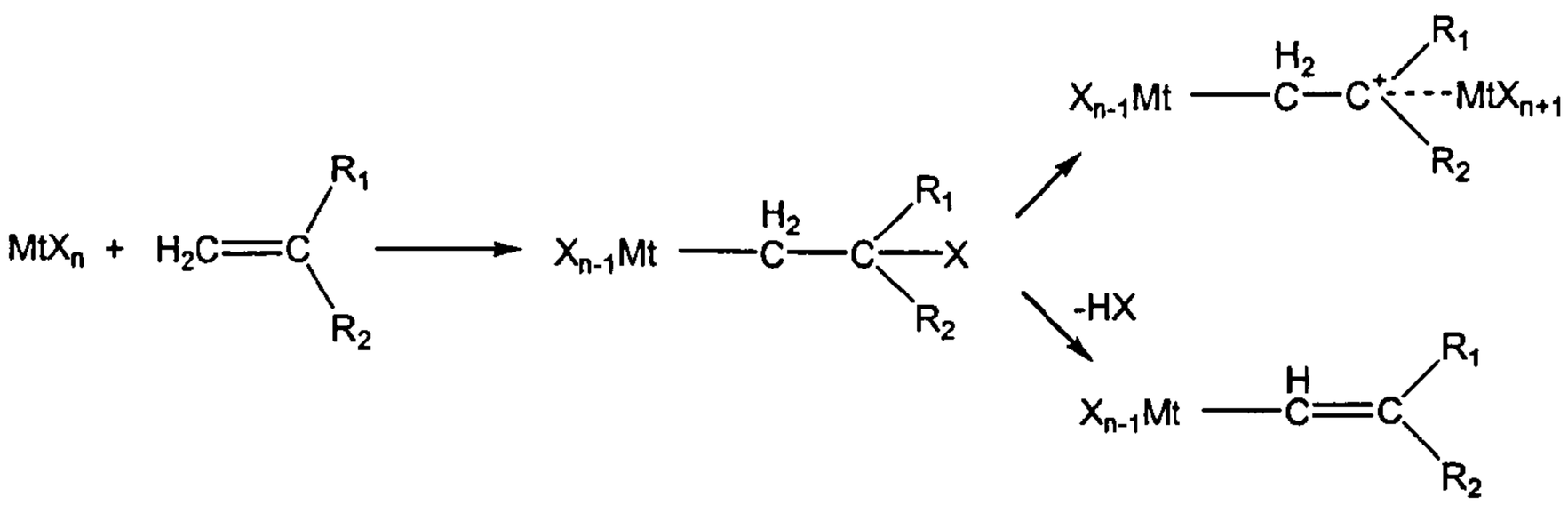
Scheme 1-2: Protonic acid initiated cationic polymerisation

The complex anion A^- of the protonic acid assists ion generation. The initiation activities of protonic acids depend on the quality of the corresponding anion or the anion's tendency to form chemical bonds with the carbon cation. When the anion is unable to form such bonds without extensive regrouping or decomposition,

the addition of the proton to the monomer can initiate a polymerisation. Solvation effects can suppress the anion reactivity and enhance the polymerisation and that is the reason that polarities of the media are very important for the protonic acids efficiencies. Stronger protonic acids lead to higher polymerisation rates and degrees of polymerisation. Generally hydrogen halide acids and sulfuric acid do not initiate alkyl-substituted olefins but they can initiate aryl-substituted olefins and vinyl ethers in polar solvents.

When such a counterion is highly nucleophilic, complexing agents such as metal salts or metal oxides must be used to immobilize the anions. These metal salts or metal oxides are actually best regarded as co-initiators.

Many researchers believe that none of the Lewis acids can initiate cationic polymerisation of olefins by themselves and the initiation requires other molecules like water or alkyl halide to form initiating ions. However, it has also been demonstrated that there are also some strong Lewis acids like boron halides [Bui, 1987; Balogh, 1994] that are capable of initiating cationic polymerisations. Some mechanisms were proposed to explain the polymerisations initiated by Lewis acids without any co-reactant. One of the mechanisms is based on a concept that initiation takes place by a process of halometalation followed by elimination of hydrogen halide or Lewis acid ionisation as shown in scheme 1-3.

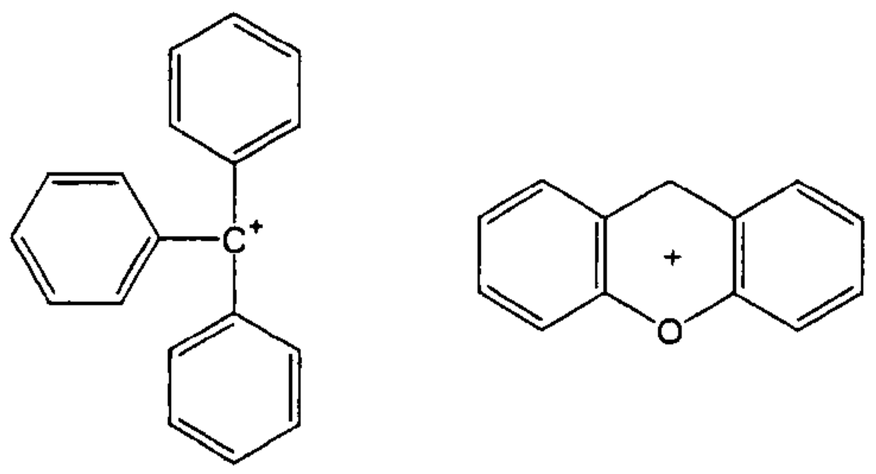


Scheme 1-3: Mechanism of Lewis acid initiation of cationic polymerisation

However, much evidence gathered to date supports the idea that it is the autoionisation of Lewis acids that initiate the polymerisation. Firstly proposed in 1948 [Korshak, 1948], the concept suggests that Lewis acids can aggregate into dimers and then autoionise and initiate the polymerisation.

Covalent esters and halides do not react directly with alkenes but need to be ionised first to give sp^2-hybridised carbenium ions to initiate the cationic polymerisation. This could because of the high proportion of charge which must be transferred to the alkene in the transition state. Lewis acids are typically used to activate dormant covalent esters and halides, as well as protonic acids. When water or other alkyl halides, esters are required as co-reactants in a Lewis acid initiated cationic polymerisation, the Lewis acid is actually present as co-initiator which complexes with water or alkyl halides for the ionisation, and water and alkyl halide are the real initiators. Lewis acids being applied in the current research in this thesis are co-initiators and the detailed mechanism will be discussed separately.

Cationic polymerisations initiated by stable cations were firstly reported by Bawn and co-workers [Bawn, 1964]. Some examples of stable cations that can initiate cationic polymerisations are the triphenylmethyl ion and xanthylium ion shown in figure 1-1.



Triphenylmethyl ion Xanthylium ion

Figure 1-1: Stable cations that can initiate cationic polymerisations

These cations form crystalline salts with anions such as ClO_4^-, $SbCl_6^-$, BF_4^- and PF_6^- etc. [Ledwith, 1974]. The concentration of cations need to be low for complete dissociation from their respective counterions. The initiation could progress via direct addition of the cation to the unsaturated system, or by hydride abstractions to fulfill cationation, or through electron transfer to form cation radicals which eventually initiate the polymerisation [Bawn, 1968]. It should also be pointed out that only strong nucleophilic olefins like alkyl vinyl ether, N-vinyl carbazole, *p*-methoxystyrene, indene and vinylnaphthalenes can be polymerised by stable cations.

Chain propagation

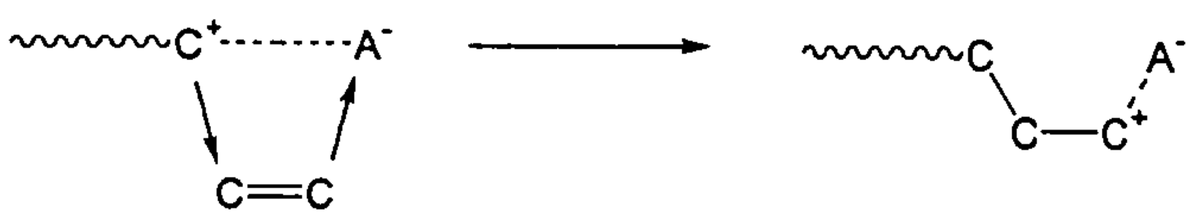
Propagation is the most important fundamental reaction of a polymerisation because it results in formation of the entire macromolecule except the end groups.

Thus the polymerisation rate, molecular weight and molecular weight distribution may be regulated if the propagation mechanism is elucidated. Also microstructures of the polymers can be more controlled.

To understand the propagation mechanism, the structure of monomer and the growing species needs to be known. The presence of several different active species which often have short lifetimes usually complicates the situation.

In carbocationic polymerisation the reactivity of the active centres generally follows their degree of ionisation. The bonds between carbocations and the counteranions can vary from a high degree of covalence to tight ion pairs, loose ion pairs and that of free, solvated ion pairs [Matyjaszewski, 1996b]. The covalent species are not active at all for chain propagation, while the reactivities of carbenium ions are similar regardless of degree of association. Free carbenium ions are apparently only 5 to 20 times more reactive than ion pairs. Chain-growth reactions with fairly tight ion pairs, that occur in the medium of low polarity, require that the monomer be inserted repeatedly between the two ions.

The ion pairs are first loosened and complexed with monomer, then the insertions complete the process. The insertions result in formation of new carbon cations and they immediately pair off with the counterions and the process continues. The mechanisms of such insertions consist of repeated push-pull attacks by the ion pairs on the double bonds of the incoming monomers [Kennedy, 1964] shown in scheme 1-4.



Scheme 1-4: The cationic propagation mechanism

The degree of association of the ion pairs depends also upon the nature of the counterion and on the temperature of the reaction medium. Completely dissociated ion pairs allow chain growth to take place free from the influence of counterions. The carbon cations simply add directly to the double bonds of the incoming monomers. Propagation rates with the dissociated ion pairs are higher than with the tight ion pairs [Pepper, 1962]. It needs to be pointed out that although the propagating free ions are

not affected by the counterions, they are still associated with polar or polarisable solvent molecules or monomers.

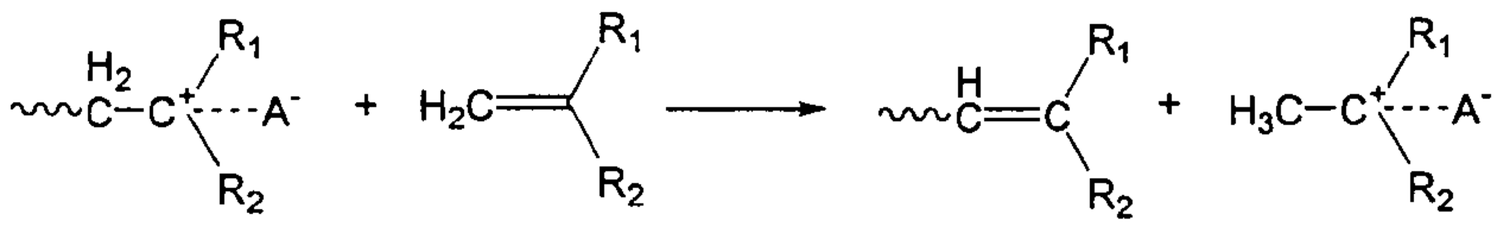
The majority of propagating chain ends in most cationic polymerisations co-initiated by a Lewis acid do not exist as carbenium ions, instead, they are dormant species such as covalent halides which are the products of reversible reactions between carbenium ions and counterions. The rate constants of interconversion between active and dormant species determine the polymers' polydispersities.

The monomers behave as nucleophiles or as electron donors during the chain propagation. Increased electron densities at the double bond increase the chain propagation rate. The polarity of the monomer substituents and steric effects both show significant effects on chain propagation. The efficiency of the counterion is related to its acid strength. In polar solvents the counterions interact only weakly with the growing cations and the steric effects become major factors in determining the courses of propagation.

When both the solvated carbocations and the paired carbocations are present in the same polymerisations, a more complicated system containing more than one propagation path will be formed. Some chains may grow without a terminal counterion as a free propagating species while other polymer chains are paired off with counterions. When more than one growing species is present during the polymerisations, the polymers obtained could show multimodal molecular weight distributions. It is reported that biomodal molecular distributions are very often observed in cationic polymerisations [Masuda, 1976; Sawamoto, 1978; Majoros, 1994]. Matyjaszewski's research indicates that bimodal molecular weight distributions are formed with free ions and ion pairs of identical reactivities but different lifetimes. The high molecular weight fraction is formed by free ions and the low molecular weight fraction is formed by ion pairs [Matyjaszewski, 1994a; Matyjaszewsk, 1994b].

Chain transfer and chain termination

When growing, carbenium ions are highly susceptible to transfer reactions by β-proton elimination and transfer of their ion pairs to monomers and thus old chains are terminated and new chains are initiated at the same time. This is usually referred to chain transfer. Chain transfer to monomer is a bimolecular reaction as shown in scheme 1-5.



Scheme 1-5: Chain transfer in cationic polymerisation

Transfer reactions generally decrease the polymer molecular weight by generating new chains from the same initiator. This does not affect the polymerisation kinetics because the concentration of growing species does not change. Chain transfer is an important chain-breaking reaction in the cationic polymerisation of alkenes.

Termination of cationic polymerisation, where the termination reactions stop the kinetic chain, is also complicated. The process can be divided into unimolecular termination and bimolecular termination.

The unimolecular rearrangement procedure involves hydrogen cleavage and recombination procedures which irreversibly deactivate the growing species. Counterions can react with propagating carbenium ions by either recombination to form a covalent bond, or by abstracting a β-proton to generate an unsaturated end group. Nucleophilic counteranions and additives tend to react by recombination, whereas basic anions favor elimination.

These terminations mentioned above not only limit the molecular weight of cationic polymerisation, but also prevent the whole system to be a living polymerisation system. However, if termination is negligible throughout the polymerisation, the propagating chains will retain their activity until the completion of monomer consumption. The electrophilic chain ends can be functionalised by controlled termination to give chain end functionalities. This kind of forced termination is also a bimolecular termination process. Impurities like water can also act as chain transferring agents or end-capping agents and terminate polymer chains. More controlled polymerisations have used inifers [Kennedy, 1983; Zsuga, 1991, Mah, 1987] as both initiator and transfer agents in cationic polymerisation.

1.2.5 Factors that affect cationic polymerisation

Solvent effect

The ionic polymerisation process is strongly influenced by the polarity of the solvent. Solvent can affect the ion pair intimacy of the active centre from covalent

bond to intimate ion pair, separated ion pair or even dissociated free ions depending on the different solvent polarity. Solvents tend to solvate cations rather than anions so that there is less difference in the reactivities of free ions and ion pairs in cationic system, whereas they are quite different in anionic systems.

All elementary reactions in cationic polymerisations suffer solvent effects. A solvation effect can suppress the reactivity of the anion and reduce the stability of the chemical bond between the carbocation and the anion and thus enhance the rate of initiation.

Evidence of a solvent effect on the carbenium reactivity is provided by stopped flow studies [Kunitake, 1979; Varion, 1992]. It was found that the carbenium ion had apparently a lower reactivity in the more nucleophilic solvent. This led to a lower chain propagation rate in 1,2-dichloroethane [Kunitake, 1979] than in dichloromethane [Varion, 1992].

It is also observed that the chain propagation is 1000 times faster in dicloromethane than in a non-polar hydrocarbon solvent, although chain propagation by carbocationic species is slightly slower in more polar solvents. The higher concentration of carbenium ions, due to the shift of the ionisation equilibrium, largely increases the rate of polymerisation.

The ionic species are more solvated in more polar solvents and collapse of the propagating ion-pairs are faster in less polar solvents. Termination reactions of the propagating carbenium ions in the presence of impurities are also accelerated in less polar solvents. Furthermore, if a solvent is too nucleophilic it can terminate the reaction itself and if too basic it will abstract β-protons.

Additive effect

Nucleophiles can affect many important events in cationic polymerisation. They are believed to have influence on initiation, propagation and chain transfer and can affect the rates of polymerisation, initiation efficiency, molecular weight and molecular weight distribution.

Through the complexation of nucleophiles with active centres, the reactivity of a conventional carbenium ion is reduced such that both the initiation and propagation rates are reduced. Being a two-step process, the initiation rate reduction is less than the decrease in the propagation rate and this leads to relatively quick initiation and slow propagation resulting in narrow molecular weight distributions. Thus well-

defined polymers are observed in systems with nucleophiles in cationic polymerisation [Lin, 1990; Xiang, 1992; Lin, 1994; Si, 1994; Kennedy, 1991b]. Also, because of the higher reduction of propagation rate, a higher initiation efficiency is obtained in these systems with nucleophiles. When the initiation efficiency is nearly 100%, the molecular weight is predictable. Chain transfer will also be found to occur when the β-protons share a higher positive charge and are of higher acidity. The deprotonation can be suppressed by nucleophiles through complexation with cationic centres and reduced the acidity of the β-protons, so that chain transfer can be reduced or even eliminated from the system.

All these influences on cationic polymerisation come from the effect of the nucleophile on the reactivity of the cation. Nucleophiles can also interact with all electrophilic species in the system, including dormant species, carbenium ions [Lin, 1990; Lin, 1994] and Lewis acids [Si, 1994; Kennedy, 1991b]. Dormant covalent species are too weakly electrophilic to react with most nucleophiles, but are known to react with the strongest ones. Weaker nucleophiles such as sulfides, esters and ethers do not react with covalent species but react readily with carbocations and form onium ions which reduce the lifetime of carbenium ions, which reduce the possibility of rearrangements at the chain end that form the stable and less reactive carbenium ions. Aoshima et al. reported the application of ether additives like 1,4-dioxane, tetrahydrofuran, diethyl ether, ester additives like ethyl acetate, methyl chloroacetate and ethyl benzoate in cationic polymerisation of vinyl ethers which produced more controlled polymerisations [Aoshima, 1995, Higashimura, 1989]. Nucleophiles can also complex with Lewis acids and the complexes are less nucleophilic than the original nucleophiles and less electrophilic than the original Lewis acids and these effects also lead to a more controlled polymerisation.

Cationic polymerisations are influenced by ion scavenger impurities like water, ammonia, amine or other basic compounds. These basic impurities assist the loss of the β-protons and enhance chain transfer. Water may act as the chain transfer agent as well as the initiator when using excessive Lewis acid [Matyjaszewski, 1997b]. Gandini has also used 2,6-di-*t*-butyl-4-methylpyridine (DBMP) as proton scavenger to diagnose the cationic polymerisation mechanism [Gandini, 1997].

Polymerisation temperature effect

Most cationic polymerisations are exoentropic (approximately –120J $mol^{-1}K^{-1}$) due to the loss of three degrees of translational freedom caused by connecting monomeric units together. To maintain a negative free energy for the thermodynamic feasibility of the polymerisation a sufficient exoenthalpy to more than compensate for the loss in entropy is required. The loss of enthalpy can be provided by isomerisation of the double bond to a single bond in the polymerisation of alkenes or by relief of ring-strain in a ring-opening polymerisation. This is one of the reasons that low temperatures sometimes favour cationic polymerisations.

Each elementary reaction is affected by temperature in different ways, sometimes resulting in overall negative overall activation energies [Corel, 1976]. The activation energies of side reactions such as chain transfer are usually higher than those of propagation and this is one of the reasons that cationic polymerisations need to be run at low temperatures to produce high molecular weight polymers. Also, chain propagation and other reactions involving carbenium ions experience significant solvent effects. Because the solvation process is exothermic, the effect of temperature can be considerable.

1.2.6 Monomers used in cationic polymerisation

In radical polymerisations and most ionic polymerisations, long chains are readily formed through addition reactions. Monomers with the general structure of $CH_2=CR_1R_2$ are susceptible to rearrangement if activated by radical or ionic initiators because of the special reactivity of the π-bond. Altering the negativity of the π-bond electron density can determine whether a radical, anion or cation will be stabilised preferentially. The choice of free radical, cationic or anionic polymerisation largely depends on the substitute in the monomer and their effect on the double bond.

In radical polymerisation the presence of electron-withdrawing substituents that reduce the electron density of the double bond facilitate the monomer being attacked by the radical, this is because the electron withdrawing effect reduces the system energy and stabilises the radical active centre. On the other hand, the electron donating groups on the carbon-carbon double bonds retard the attack of radical to monomer and the formation of active centres, despite the fact that phenyl and vinyl groups in styrene and butadiene are electron donating groups, but the conjugation

effect stabilises the active centres and both the two monomers are very easy to perform radical polymerisation [Yun, 1995]. Electron-withdrawing substituents are required to activate olefins in anionic reactions.

Alkenyl, alkoxyl and phenyl groups tend to increase the nucleophilicity of the alkene by donating electrons and this encourages cationic polymerisations. In addition during the cationic polymerisation the active centres are resonance stabilised. Monomers like styrene and 1,3-butadiene can undergo both cationic and anionic polymerisations because the anionic species can also be stabilised.

Typical vinyl monomers for cationic polymerisation are vinyl ethers, *N*-vinylcarbazole, styrenes and 1,1-disubstituted alkenes such as isobutylene and α-methylstyrene.

Cationic polymerisation of a series of alkyl vinyl ether monomers were studied in detail and reactions rates were measured in a conventional polymerisation system. The electron-donating group—alkoxy group enhances the electron density of the double bond and makes the monomers act as nucleophiles towards the cationic centre during chain propagation. Isobutyl vinyl ether, ethyl vinyl ether and methyl vinyl ether are among this group and the possibility of correlating reactivity with structure were investigated by Ledwith et al. [Ledwith, 1975]. Compared with ethyl vinyl ether and isobutyl vinyl ether, methyl vinyl ether presented a lower propagation rate constant and higher activation enthalpy. In the selected polymerisation system the approximate relative chain propagation rate constants of MVE, EVE and iBVE are 1:10:48 and the suggested reason for this is that MVE's special conformational property leads to a greater degree of steric hindrance to the incoming electrophile.

PMVE interests people because it exhibits a Lower Critical Solution Temperature (LCST) and it has been synthesised as a temperature responsive block in block copolymers [Kwei, 1974; Nishi, 1975]. The living cationic polymerisation technique was applied in the synthesis of various linear or non-linear copolymers with the PMVE block, including the amphiphilic PIB-b-PMVE [Bae, 1998; Pernecker, 1992a; Pernecker, 1992b], PS-b-PMVE [Ohmura, 1994; Hashimoto, 1997], and the dihydrophilic block of methyl triethylene glycol vinyl ether with methyl vinyl ether, PMTEGVE-b-PMVE [Forder, 1996].

1.2.7 Lewis acids

Lewis acids can complex with initiators in polymerisation to reduce the electron density of the active centre, so that the electron acceptor is enhanced. As mentioned above, Lewis acids are mostly used in a binary initiation system as activators or co-initiators. In this way Lewis acids regulate both the initiation and polymerisation rates and give a faster and therefore more efficient initiation so providing better control over the polymerisation rate, the number of chains generated and their molecular weight.

The polymerisation rate depends on the equilibrium position between carbenium ions and the corresponding covalent adducts. The molecular weight distribution is determined by the dynamics of the equilibrium, particularly the rate of deactivation of active to dormant species. If this exchange rate is slow in comparison to propagation, the distribution will be broad or sometimes even multimodal. In contrast, a Poisson distribution of $M_w/M_n \cong 1$ can be approached if the exchange rate is faster than the propagation. Thus, the lability of the Lewis acid's ligands and their relative nucleophilicities and basicities are important in controlling the polymerisation. Ligands may exchange with the leaving group of the original initiator.

Very strong Lewis acid will not be optimal if they lead to exceedingly fast and uncontrolled polymerisations. Moreover, collapse of the ion pair involving very strong Lewis acids is irreversible due to the very strong carbenium-counterion bond, resulting in termination. Thus, the overall polymerisation rates in some systems may be lower with strong Lewis acids than with weak Lewis acids. Very strong Lewis acid may form complexes even with weak nucleophiles such as solvent, monomer or an additive. These complexes are relatively inactive, leading to overall rates of polymerisation that are lower than those observed with weaker Lewis acids which do not form such complexes.

When the activator is too strong, a deactivator may also be required to control the polymerisation. Deactivators such as salts and nucleophiles interfere with the growing species and are not directly involved in initiation.

Lewis acid acidities have been compared in former researches, for example, in the polymerisation of isobutylene at -78°C. Lewis acids were rated according to the efficiencies shown as follows [Evans, 1947].

$BF_3 > AlBr_3 > TiBr_4 > BBr_3 > SnCl_4$

Many Lewis acids were applied in the cationic polymerisation of vinyl ethers. Among them, $TiCl_4$ is frequently used due to its high Lewis acidity [Deng, 2001; Sawamoto, 1995; Faust, 1991] and often in combination with protonating agents such as hydrogen halide or carboxylic acids. $TiCl_4$ forms a dimer that is more reactive than its monomeric Lewis acid. Lewis acidity is quite varied due to this dimerisation and the complexation with monomer—it was observed that mixtures of $TiCl_4$ with alkenes are often colored—apparently due to weak complexation.

$SnCl_4$ was the first Lewis acid that has been applied for cationic polymerisations [Deville, 1839]. It is used most often in combination with alkyl chlorides and esters preformed by the reaction of the corresponding protonic acid with monomer. $SnCl_4$ can complex with chloride anion and become a weaker Lewis acid [Lin, 1993; Katayama, 1998] such as $SnCl_5^-$ and $SnCl_6^{2-}$ under the presence of chloride-anion donors (for example, *n*-Bu_4NCl is an effective chloride-anion donor).

$SnBr_4$ is a much weaker Lewis acid than $SnCl_4$ but its ligands are more labile and therefore it successfully catalyses cationic polymerisations and generates a well-defined system [Kamigaito, 1993; Hashimoto, 1998].

$ZnCl_2$ is relatively weak Lewis acid that can initiate the most reactive monomers such as N-vinyl carbazole, vinyl ethers and alkoxystyrenes. Poor solubility of this Lewis acid in halogenated hydrocarbons has affected its usage.

1.2.8 Kinetics of cationic polymerisation: a review

Kinetic feasibility of cationic polymerisation requires a site for attack by reactive centres generated by the initiator. For alkene monomers the double bond provides such a site. The monomers need to be nucleophilic and reactive enough and capable of stabilizing the resulting positive charge. Many factors affect the reaction rate. For example, monomer substituents influence the electron density of the double bond during the polymerisation and affect the resonance stabilisation of the chain end carbocation. The effect of counterions, additives, solvents and reaction temperature also have influences on reactivities.

A series of model studies by Mayr et al. on the reactions of carbocations with nucleophiles provide valuable information for the design of carbocationic polymerisations [Mayr, 1997]. Their research provide a guide on how to select a binary initiation system, the relative alkene reactivites they reported show the possibility of selecting comonomers, hydride transfer abilities of some hydride donors

give the possibility of predicting the transfer reactions. Their research indicate that the reaction rate of carbocation with alkene is generally independent of the nature of the complex counterion and that free and paired carbocations react with equal rates [Mayr, 1996].

Kinetic measurements require determination of the concentration of all reagents and active species as a function of time. The rate of polymerisation is defined as the rate of monomer consumption, which depends on the concentration of monomer and active centres. Three methods have been developed to obtain more accurate rate constants for cationic polymerisation. They are based on direct measurement of the concentration of growing species by rapid spectroscopic techniques [Varion, 1992; Pepper, 1974], on systems initiated by γ-irradiation [Goineau, 1977] and on systems initiated by trityl salts [Sauvet, 1974] which are consumed slowly. Despite the disadvantages of all three methods they provide consistent carbocationic propagation rate constants ($k_p \approx 10^{5\pm 1}$ $mol^{-1}L\ sec^{-1}$at 0°C)

Monomer consumption can be measured by spectroscopic techniques including NMR, UV, IR and by chromatography techniques, or by dilatometry, calorimetry and gravimetry. The routine use of NMR to study model compounds has not yet been extended to polymerisation studies due to the very low intensity of resonances from the growing carbenium ions.

A typical kinetic discussion on cationic polymerisation of alkene monomers in a binary initiation system is listed as follows:

The cationic initiation procedure can generally be divided into two steps, i.e., ion generation and cationation. These two step initiations can be expressed as:-

$$RX + M_tY \xrightarrow{kig} R^+M_tYX^-$$

$$R^+M_tYX^- + M \xrightarrow{kc} RM^+M_tYX^-$$

where RX is the initiator, M_tY is the Lewis acid, M is the monomer, k_{ig} and k_c are ion generation and cationation rate constants respectively. The term $R^+M_tYX^-$ is for the complex formed from the initiator with the Lewis acid.

When the ion generation is the key step of the initiation process, the initiation rate can be expressed as equation 1-1:

$$R_i = -\frac{d[I]}{dt} = k_{ig}[RX][M_tY] \quad \textbf{(1-1)}$$

where R_i is the initiation rate, I is the initiator, *[RX]* is the initiator concentration and *[M_tY]* is the Lewis acid concentration.

On the other hand, when the cationation become the rate controlling step, i.e., when $k_c << k_{ig}$, then the initiation rate is: -

$$R_i = -\frac{d[I]}{dt} = k_c[R^+M_tYX^-][M] \quad \textbf{(1-2)}$$

where *[M]* is the monomer concentration, and *[$R^+M_tYX^-$]* is the concentration of active species.

Chain propagation occurs according to the following mechanism: -

$$RM_n^+M_tYX^- + M \xrightarrow{kp} RM_{n+1}^+M_tYX^-$$

The monomer consumption includes two parts: a small amount that is consumed through cationation and the majority which is consumed through chain propagation. The chain propagation rate is: -

$$R_p = k_p[RM_n^+M_tYX^-][M] \quad \textbf{(1-3)}$$

where R_p is the chain propagation rate, and k_p is the chain propagation rate constant.

Chain transfer to monomer can terminate an old chain and a new chain is initiated at the same time. Termination reactions can occur by spontaneous termination, combination with the counterion, or by transferring to a transfer agents or, by being capped by an end-capping agent, E. The events may be expressed as:-

Transfer to monomer: $RM_{n+1}^+M_tYX^- + M \xrightarrow{ktr} RM'_{n+1} + M^+M_tYX^-$

Spontaneous termination: $RM_{n+1}^+M_tYX^- \xrightarrow{kt} RM'_{n+1} + H^+M_tYX^-$

where $k_{tr,}$ and k_t are the chain transfer rate and the spontaneous termination rate constants respectively. Spontaneous termination and chain transfer to monomer, as follows:- forms a chain-end double bond

Combining with the counterion: $RM^{+}_{n+1}M_tYX^- \xrightarrow{kt'} RM^{+}_{n+1}X^- + M_tY$

End capping: $RM^{+}_{n+1}M_tYX^- + E \xrightarrow{k_{cap}} RM_{n+1}E^+M_tYX^- \rightarrow RM_{n+1}E'$

Among them the end-capping rate is: $R_e = -\frac{d[E]}{dt} = k_{cap}[RM^{+}_{n+1}M_tYX^-][E]$ **(1-4)**

where k_{cap} is the end-capping rate constant and *[E]* is the end-capping agent concentration.

1.2.9 Controlled/Living cationic polymerisation

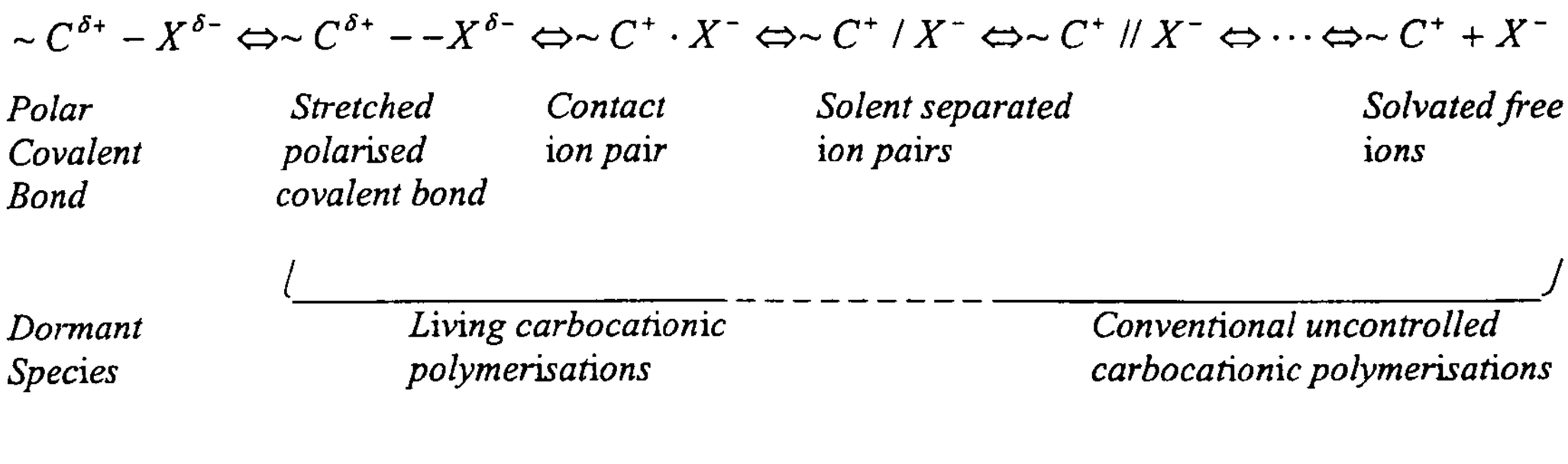
A controlled polymerisation system can be produced by anionic polymerisation, cationic polymerisation, group transfer metathesis, coordination polymerisation using Ziegler-Natta catalysts and radical polymerisation, giving well-defined polymers with controlled molecular weight, polydispersity and terminal functionality. Controlled systems provide an effective method for well-defined polymers with reduced side reactions.

If the polymerisation conditions are carefully controlled a terminationless or *quas*i-terminationless polymerisation system can be prepared which is known as a living polymerisation system. The chain propagation is maintained because the propagating centres are of low reactivity and chain transfer and termination are suppressed. In such systems, the continuous slow addition of monomer can extend the lifetime of the propagating species.

The controlled cationic system means more than just regulation of molecular weights and molecular weight distribution, it also means the control of other structural factors like end groups, pendant groups, sequence, steric structure, three-dimensional or spatial shape etc.. This allows the introduction of functional groups into specific positions on the polymers to give well-defined architectures leading to a wide variety of polymers of synthetic interests. These include polymers with pendant functional groups, block copolymers, polymers with terminal functional groups, polymers and oligomers with regulated sequences of repeat units, star-shaped or multi-armed polymers, graft polymers, macrocyclic polymers and amphiphilic polymers.

Many potentially useful and well-defined new materials have been formed from controlled cationic polymerisations. Among them well-defined polyisobutylenes, hydroxy-telechelic polyisobutylenes and highly branched butyl rubbers are already commercially or semicommercially available.

Many efforts have been made to clarify the intrinsic principles of living polymerisations. Winstein et al [Winstein, 1956] first presented the proposal that different types of ionic species, each with distinct reactivities, may participate in reactions involving cationic intermediates. As shown in scheme 1-6 below, Winstein and co-workers proposed that four species are in equilibrium, including covalent electrophiles, contact ion pairs, solvent-separated ion pairs and free ions.



Scheme 1-6: The Winstein spectrum of ionicities of propagating species in carbocationic polymerisation [Kennedy, 1991a]

Kennedy et al. discussed the relationship of livingness of cationic polymerisation with these species [Kennedy, 1991a]. Kennedy's research indicated that it is difficult to define where the species may lead to living systems or where they may lead to conventional uncontrolled processes. But in any event, living polymerisations are more prone to arise with species on the left of the spectrum and conventional non-living polymerisations come from species on the right side of the spectrum. More clues for obtaining a living system can be gained from this Winstein spectrum. If a transformation of the right side active species to left-side propagating species can be made, livingness might arise. For example, the addition of a common anion to a conventional non-living polymerisation could increase the concentration of left side less reactive species so that the conventional polymerisation can become living. This method is now widely used to produce a controlled or living polymerisation.

Former studies also showed that living vinyl ether polymerisation systems have the following properties [Nuyken, 1997] which can be used to judge whether a polymerisation is living or not.

- the initiation is spontaneous
- the molar mass is controlled by the proportion of monomer and initiator concentration.
- the molar mass increases with conversion
- the molar mass increases by sequential addition of monomer
- the molar mass distribution is narrow
- the well-defined distribution and controlled termination allows the synthesis of macromonomers and telechelics.

1.2.10 Potential application of cationic polymerisation

Cationic polymerisations enable the synthesis of unique polymer structures and can be widely applied in commercial materials production. A detailed review on this topic was given by Varion and co-worker [Vairon, 1996]. More than 36 commercial polymers and copolymers have been produced either via alkene, or heterocyclic monomer cationic polymerisations [Pazur, 1998]. Among them polybutenes, polyisobutenes, hydrocarbon resins and polyvinyl ethers are formed via vinyl polymerisations.

Polybutenes are non-staining, stable at high shear and demonstrate excellent lubricating ability. They are therefore used as additives in lubricants, fuels, caulks, food wrapping, adhesives, coatings, personal care products, concrete sealers, rubber modifiers and plasticisers. Poly(butenylsuccinic anhydride) produced from chain end modification of polybutenes have the special advantage of corrosion-inhibiting while used as lubricants or additives. The applications of low molecular weight polyisobutenes (PIB) are quite similar to those of polybutenes. Medium and high molecular weight PIBs are used as sealants, adhesives, flexibility improvers for waxes and as impact additives for thermoplastics. Butyl rubbers are crosslinked linear, random copolymers based on isobutene and small amounts of isoprene. Their properties of low rebound resilience, excellent damping characteristic, impermeability to small molecules and low toxicity allow them to be used as inner tubes, curing bladders, pharmaceutical stoppers, chewing gum formulations, auto parts, railway pads, wires and cables, tank lining, hose, belting, packaging film and adhesives.

Hydrocarbon resins have no commercial applications alone and must be used as modifiers in other materials as processing aids, extenders and plasticisers for resins and rubbers. They are also used in paints, coatings, adhesives and rubber compounding.

In the mid 1970s, Crivello and Lam discovered photoinitiation of cationic polymerisation and thus a new coating technology is developed. They found that diaryliodonium salts efficiently induce proton-initiated polymerisation of olefins and epoxies under UV radiation. UV curing is widely applied in the coating industry, especially for large objects [Crivello, 1976; Hua, 2001; Crivello, 1996].

Vinyl ether polymerisations by radical polymerisation are slow and cationic polymerisations are much more efficient and preferred for homopolymer productions. Vinyl ether polymers are used as non-migrating tackifiers in adhesives, viscosity index improvers in lubricants and plasticisers in coatings, films and elastomers.

Living cationic polymerisation of vinyl ethers can be used to prepare polymers with special properties like narrow polydispersity. Amphiliphilic block copolymers have been synthesised by the sequential polymerisation of the hydrophilic methyl vinyl ether (MVE) and the hydrophobic octadecyl vinyl ether (ODVE) which has emulsifying properties for water and decane mixtures. End-capping of living polymers with hydroxyethyl acrylate [Goethals, 1998; Lievens, 1996] lead to end-functionalised polymers which can be used as macromonomers. PolyODVE-b-poly(Bu-acrylate) networks display phase separation and due to the crystallinity of the polyODVE domain, these materials also show shape memory properties.

Tsubokawa et al. [Tsubokawa, 2000] applied carboxyl groups on a carbon black surface, together with ethylaluminum dichloride to initiate the living-like cationic polymerisation of isobutyl vinyl ether in the presence of 1,4-dioxane. Termination of the polymerisation produced the grafted PiBVE on the carbon surface. It is possible to control the molecular weight of the surface graft polymer in a living cationic or anionic polymerisation. Armes and co-workers [Patrickios, 1996; Patrickios, 1997] have explored using living cationic polymerisations of vinyl ethers to prepare water-soluble diblock and triblock copolymer or amphiphilic block copolymer. They have also explored an alternative route to obtain polymer with water solubility—poly(vinyl alcohol)s were synthesised via living cationic polymerisation of ethyl vinyl ether followed by a series of modifications [Forder, 1995].

1.3 *Ab initio* chain end functionalisation

1.3.1 Chain end functionalisation and end-capping

When functional groups are introduced during the initiation [Shohi, 1991a; Shohi, 1991b; Sawamoto, 1991] or termination [Sawamoto, 1987a; Sawamoto, 1987b; Hashimoto, 1990; Fukui, 1993a] steps, the chain end functionalities can be obtained. The initiator becomes the macromolecule's head group whilst the terminator becomes the end-group. If transfer agents [Zsuga, 1991; Kennedy, 1983] are used, this will affect the functionalities of both ends. Most functional groups being introduced during initiation procedure are capable of reacting with the active species and must be protected. For example, hydroxy groups can be introduced by the use of a silyl ether-protected initiator, and amino groups can be introduced by using the phthalimide derivatives. The functionalised polymers or oligomers can go through further reaction or polymerisation to prepare block copolymers, graft copolymers or polymeric networks.

Researches on end-capping in cationic polymerisation were carried out in living systems. In Faust's research, when 1,1-diphenylethylene was applied as the end-capping agent in living cationic polymerisation of isobutylene, only monoaddition occurred even when a 9-fold excess of end-capping agent was used [Hadjikyriacou, 1995]. Sawamoto's group applied methacryloxy($CH_2=C(CH_3)COO^-$), acetoxy (CH_3COO^-) and allyl ($CH_2=CH_2CH_2^-$) substituted organosilicon compounds to quench the living polymerisation of styrene and gave a chain end functionality of 0.9, whilst bases like methanol, benzylamine, diethyl sodium malonate and sodium methoxide, as well as (trimethylsilyl)phenyl, failed to attach to the living chain end [Miyashita, 1994].

The requirements for an effective end-capping reagent have been summarised [Ando, 1998]: the quenching reaction should be quantitative, selective and specific toward the growing ends without side reactions, such as degenerative chain transfer, anhydride or proton abstraction; the reaction should be reasonably faster than the concurrent propagation; the terminal residue from the quencher should be connected to the ω-end through stable covalent linkages that are able to withstand the environment of the subsequent workup and polymer recovery procedures; and

preferably, the terminal group thus generated can be spectroscopically quantified by NMR, UV/visible, MALDI-TOF MS or other methods.

1.3.2 *Ab initio* chain end functionalisation

End-capping in various polymerisations that have been reported in the literature being recovered all occurred at the end of the polymerisation when the monomer is nearly consumed. The idea of *ab initio* chain end functionalisation has not been reported before.

When an end-capping agent is added to the system at the beginning of polymerisation, it competes with the monomer to cap and terminate the polymer chain and give chain end functionality. If the end-capping rate is controlled at a certain rate that allows most of the monomer to be consumed, but also suppresses other side reactions, this polymerisation process is *ab initio* polymerisation and chain end functionalisation. This is a more complicated polymerisation system than formerly described because of the competition by monomer and end-capping agent for the propagating chain end. Apart from those requirements for normal end-capping agents, there are also requirements for having the suitable reaction rates with the growing active centres, which lie between the chain propagation rates and side reaction rates.

Silyl enol ethers were chosen as *ab initio* end-capping agents in the cationic polymerisation of vinyl ethers. Silyl enol ethers were formerly applied as end-capping agents in the living cationic polymerisation of vinyl ethers by Sawamoto's group in the 1990s. Up to tetra-functional silyl enol ethers were used to cap the living chain ends and star shape polymers were obtained [Fukui, 1993a; Fukui, 1993b; Fukui, 1994a; Fukui, 1994b; Fukui, 1995; Fukui, 1996a; Fukui, 1996b]. Also in another research group 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene and 1-cyclohexenyloxy-trimethylsilane were successfully applied as end-quenching agents in the living cationic polymerisation of isobutylene [Hadjikyriacou, 1995]. Close to quantitative end-quenching was achieved in the living cationic polymerisation of isobutylene at -80°C in CH_3Cl/n-hexanes 40/60 vol./vol. with $TiCl_4$ as Lewis acid.

End-capping with silyl enol ethers was also reported by Tsuyoshi Ando in 1998 when 1-phenyl-1-(trimethylsilyloxy)ethylene and 1-4-(methoxyphenyl)-1-(trimethylsilyloxy)ethylene were added to the living radical polymerisation of methyl methacrylate with the binary initiating system of dimethyl 2-chloro-2,4,4-trimethylglutarate and an organo Ruthenium salt ($RuCl_2(PPh_3)_3$). In their experiment

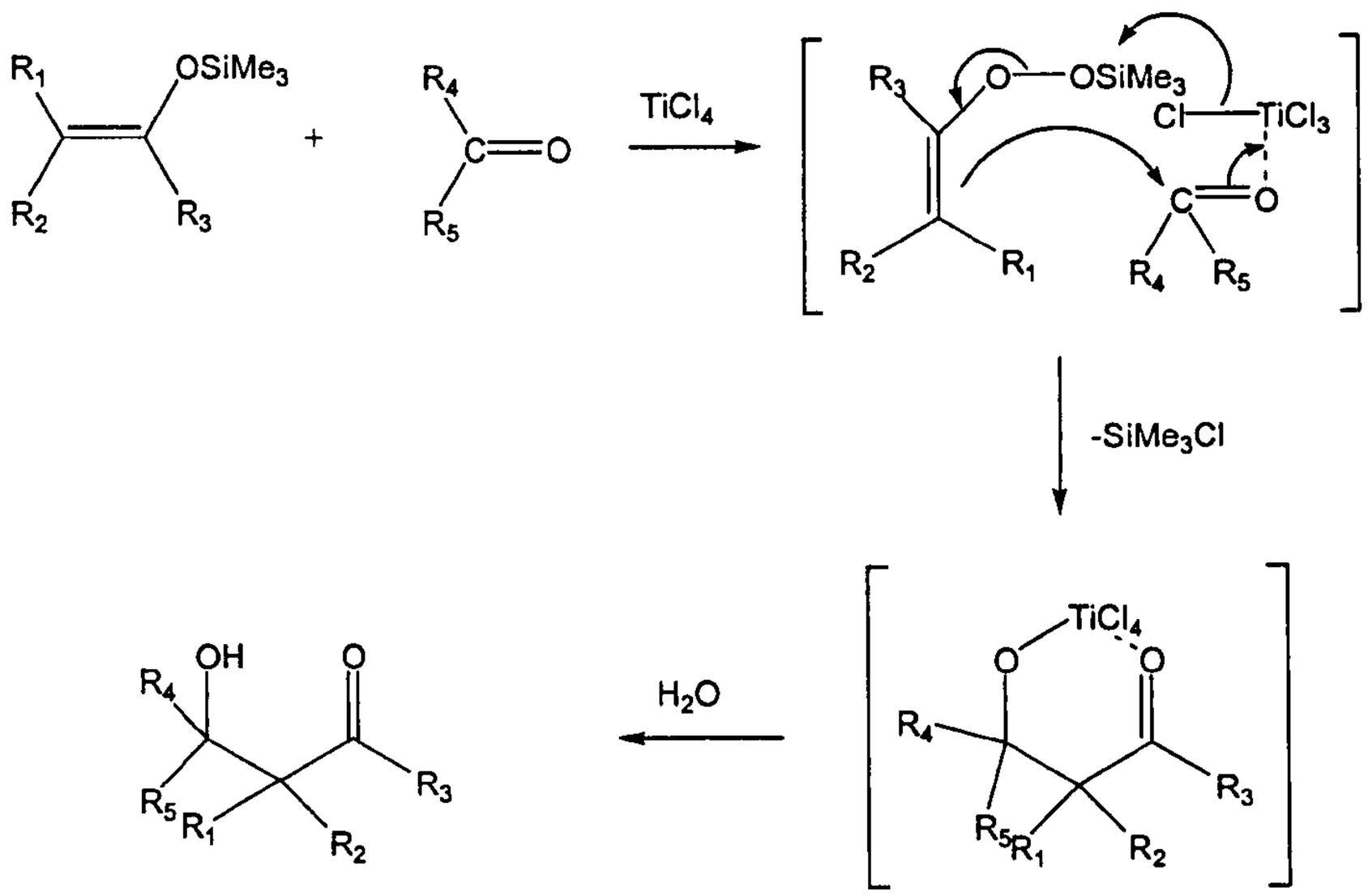
the silyl enol ethers were added at 50% monomer conversion and from the final monomer conversion it could be deduced that the quenching reaction of silyl enol ethers with the radical species is much faster than the radical chain propagation [Ando, 1998].

1.3.3 Alkylation reactions of silyl enol ethers and the Mukaiyama-Aldol reaction

The electron-rich double bonds in enols react with electrophiles in a similar way that alkenes do. Furthermore, silicon does not have a strong electron-negativity, and the presence of three attached electron-donating methyl groups, make the trimethyl silyl group strongly electron-donating. Also the oxygen connected to the double bond donates a lone-pair of electrons through a resonance effect and this makes the enol more reactive.

Silyl enol ethers, as neutral nucleophiles, are alkylated by S_N1-reaction electrophiles in the presence of Lewis acids. Enamines are among the most powerful neutral nucleophiles and they react spontaneously with alkyl halides. Silyl enol ethers, however, are less reactive and so they require a more potent electrophile to initiate the reaction whilst carbocations can be generated *in situ* by abstraction of a halide or other leaving group from a saturated carbon centre by a Lewis acid. The best alkylating agents for silyl enol ethers are tertiary alkyl halides: they form stable carbocations in the presence of Lewis acids such as $TiCl_4$ or $SnCl_4$.

Aldol condensation has long been recognised to be one of the most versatile synthetic tools in organic chemistry. However, the aldol products always contain di-, poly- or self-condensation products and this frequently limits the utilisation of this otherwise efficient reaction due to the ordinarily difficult separation of a desired product from the reaction mixture [Mukaiyama, 1974a]. Many efforts were made to alleviate this difficulty [House, 1973; Wittig, 1970], including Mukaiyama and co-workers' research on the new cross-Aldol reaction of silyl enol ethers with carbonyl compounds [Mukaiyama, 1973; Mukaiyama, 1974a]. Their research demonstrated that silyl enol ethers, prepared from various carbonyl compounds, react with aldehydes and ketones in the presence of $TiCl_4$ under mild conditions to give mono-methylol cross-Aldol addition products as shown in scheme 1-7.



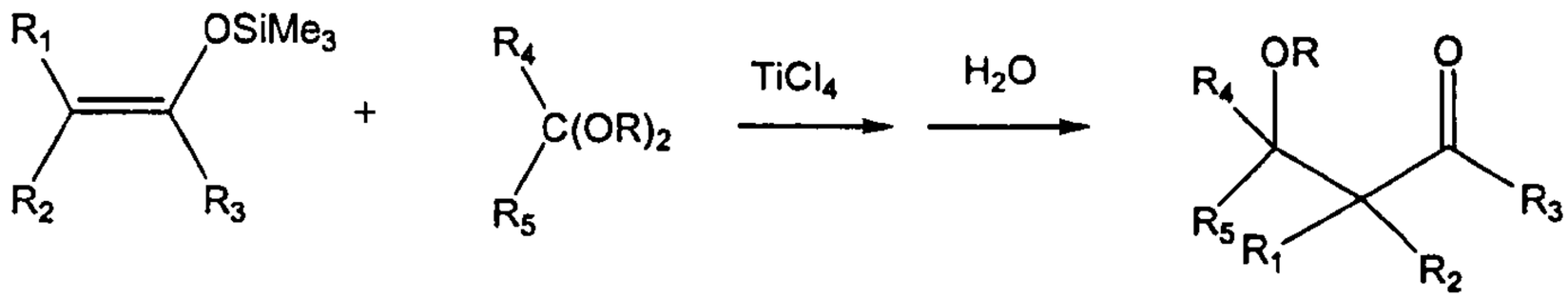
Scheme 1-7: Mukaiyama-Aldol reaction

Various Lewis acids were proved to be able to catalyse this new Aldol reaction, including $SnCl_4$, $ZnCl_2$, $AlCl_3$ and BCl_3 with different product yields. Dichloromethane was shown to significantly favour the reaction and gave the best yields whilst the desired product could not be obtained in THF and diethyl ether and gave a low yield in *n*-hexane and benzene [Mukaiyama, 1974a].

At the low temperature of -78°C the reaction of silyl enol ether with aldehydes gave excellent yields whilst at room temperature this reaction gave poor yields. On the other hand, reaction of silyl enol ethers with ketones only occurs at 0°C or room temperature.

Mukaiyama's research shows that the reaction of silyl enol ethers with aldehydes proceeds more rapidly than with ketones or esters and that silyl enol ethers selectively react with aldehyde functions in preference to ketone in the presence of $TiCl_4$ at low temperatures.

Furthermore, silyl enol ether can react smoothly with acetals or methyl orthoformate at low temperatures in the presence of $TiCl_4$ and gave β-alkoxy ketones or β-keto acetals in good yield as shown in scheme 1-8 [Mukaiyama, 1974b].

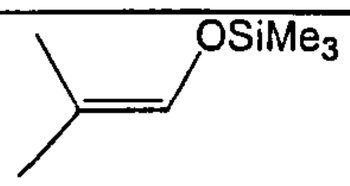
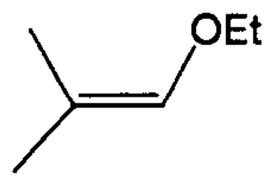
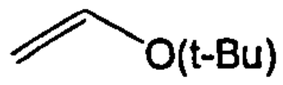
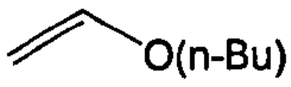
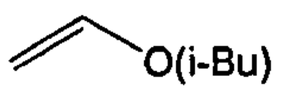
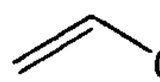


Scheme 1-8: Reaction of silyl enol ethers with acetals

1.3.4 *Ab initio* end capping by silyl enol ethers

The idea of *ab initio* end-capping of silyl enol ethers is also based on Mayr and co-workers' fundamental research on the reactions of carbocations with nucleophiles. Relative reactivities of alkyl vinyl ethers and silyl enol ethers can be compared via similar model reactions with electrophiles. Table 1-1 shows the rate constant data Mayr and co-workers provided [Bartl, 1991].

Table 1-1: Second-order rate constants for the reactions of *(p*-$ClC_6H_4)_2CH^+$ with π-nucleophiles in acetonitrile at 20°C

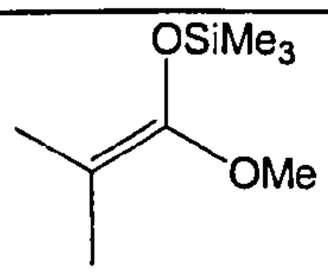
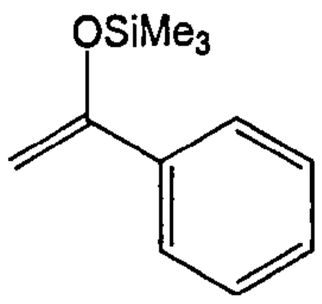
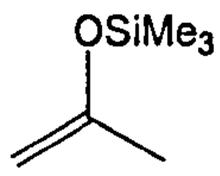
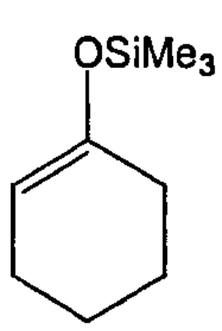
Nucleophile	k_2 L $mol^{-1}sec^{-1}$	Relative reactivity
	1.5×10^9	8.8
	2.2×10^9	12.9
	4.2×10^8	2.47
	2.0×10^8	1.2
	1.9×10^8	1.1
	1.7×10^8	1.0

It can be seen from the table that silyl enol ether and alkyl vinyl ether with similar structure have similar reactivities, and that in general, alkyl vinyl ethers have second-order rate constants close to those of silyl enol ethers. Mayr and co-workers

presented the reaction rates of model reactions of silyl enol ethers with certain cations. A weak electrophile [(p-Me_2N-C_6H_4)CH^+] was used to attack the donor-substituted double bond of silyl enol ethers. The relative reactivities of silyl enol ethers can be given from their second order rate constants as shown in table 1-2. Three out of four silyl enol ethers in the table were applied in the current *ab initio* chain end functionalisation research and different relative capping reactivities were observed. Mayr's results indicate that (1-methoxy-2-methyl-propenyloxy)-trimethyl-silane (**SEE 4**) is an stronger nucleophile than methanol [Mayr, 1994a].

Furthermore, silylated enol ethers rapidly desilylate and the carbonyl bond is formed after the electrophilic addition. Silyl enol ethers can in this way prevent further polymerisation and may thus be applied as end-capping agents in our *ab initio* cationic polymerisation.

Table 1-2: Second-order rate constants for reactions of silyl enol ethers with (p-Me_2N-C_6H_4)CH^+ in DCM at 20°C [Patz, 1993; Mayr, 1994a; Mayr, 1994b]

Silyl enol ether	Applied as	k_2 L $mol^{-1}sec^{-1}$	Relative reactivity
	SEE 4	8.02×10^{1}	418
	SEE 2	1.73×10^{-1}	9
	-	3.53×10^{-2}	2
	SEE 6	1.92×10^{-2}	1

1.4 Mass spectrometric analysis of oligomers

1.4.1 General principles of MALDI-TOF MS

Matrix Assisted Laser Desorption Ionisation Time-of-Flight Mass Spectrometry (MALDI-TOF MS) is applied in analysing the chain end functionalities of oligomers. MALDI is a "soft" ionisation process that produces molecular ions from large nonvolatile molecules with minimum fragmentation [Wu, 1998]. It was developed to analyse biomolecules such as peptides, proteins, oligonucleotides and polysaccharides, and was later applied to analyse synthetic polymers. Both molecular weight and structural information can be obtained using this technique.

Unlike chromatographic techniques, MALDI-TOF MS can give an accurate absolute molecular weight instead of a relative molecular weight which is normally obtained via Size Exclusion Chromatography (SEC) using polymer standards, as well as providing information on polymer composition and chain end structure, MALDI-TOF MS can separate a series of different polymer chains with similar chain size which is impossible for conventional chromatographic techniques, and it also gives information on detailed polymerisation procedures and side reactions etc..

Table 1-3 lists the comparison of MALDI-TOF MS with some of the conventional polymer characterisation techniques. MALDI-TOF MS requires much less sample than the conventional techniques, with only picomole to femtomole amounts of material required to give a well-resolved mass spectrum. MALDI-TOF MS is also a quick technique to obtain the accurate molecular weight information of a polymer sample in a few minutes. Unlike SEC, MALDI-TOF MS is not dependent of polymer structure. With rigid polymers SEC can result in seriously erroneous molecular weights. This problem, together with the issues of solvent or column incompatibilities, is avoided when MALDI is applied.

Molecular mass resolution decreases for very high molecular weight polymers using MALDI but for low molecular weights it works very well, whilst SEC does not work well for low molecular weight polymers. The solid MALDI sample is not always homogeneous and the large size molecules are more difficult to desorb from the sample plate than small molecules. Both of these factors suggest that MALDI can not comprehensively express the distribution of polymer sample and that conventional SEC is more accurate for information on molecular weight distribution. In addition

MALDI-TOF MS characterisation of synthetic polymers depends on the chemical structure of the polymers and successful sample preparation.

Table 1-3: Comparison of MALDI-TOF MS with conventional polymer characterisation

Technique	Absolute M_n	Relative M_n	Absolute M_w	Relative M_w	End-group	Structure	Purity	PD
MALDI-MS					+	+	+	
SEC		+		+			(+)	+
NMR	+				+	+	+	
IR	(+)				(+)	+	+	
Elemen. analysis	(+)				(+)	+	+	
Light Scattering			+					
Osmometry	+							
Titration	+				+			

Tanaka et al. first reported laser desorption of intact polymer molecular ions in 1988 [Tanaka, 1988]. A distribution of sodium cationised oligo(propylene glycol) and oligo(ethylene glycol) ions were obtained. Reported analysable polymers are expanding rapidly and so far the following polymers analysable by MALDI techniques [Danis, 1996a] are: water soluble polymers, such as poly(acrylic acid), poly(ethylene glycol); polar organic-soluble polymers like poly(methyl methacrylate); nonpolar organic-soluble polymer like polystyrene and poly(vinyl chloride), polyethylene; low solubility polymers such as cured polyimide. The most difficult polymer samples are the low solubility polymers. Non-soluble polymers are generally not analysable by MALDI because a mixture of matrix and analyte cannot be prepared if both do not fully dissolve in the common solvent [Wu, 1998].

A typical MALDI-TOF MS analysis of the oligomer sample is described as follows. The sample to be analysed is mixed with the molar excess of matrix material

and then the resultant solution is allowed to evaporate on a flat stainless steel target. The target is introduced into the vacuum system of the instrument and allowed to pump down. A fast laser pulse irradiates the target producing a burst of ions, which are accelerated in an electric field and fly down to the detector. The lighter ions fly faster and so reach the detector before the heavier ions. By measuring the time of flight of an ion and using appropriate calibration we get a measure of its molecular weight.

1.4.2 Various ionisation methods in general

Various procedures are used to form gas phase ions from molecules, depending on the physical state of the analyte. Positively or negatively charged ions, radical cations or protonated molecules can be produced by different ionisation methods. These ionisation methods can give different degree of internal excitation of the molecules. The internally excited molecules can then dissociate and produce fragment ions that reveal details of the molecular structure.

The major ionisation methods used for organic and biological compounds include: Electron ionisation (EI); Chemical ionisation (CI); Desorption ionisation (DI); and Spray ionisation (SI). Because these ionisation methods are based on different principles and different ion chemistry, they yield complementary information, so that it is very important to obtain more than one type of spectrum for the unknown compound.

Choosing the correct ionisation method depends on the physical state, volatility and thermal stability of the sample. EI is the oldest and simplest ionisation method. As a purely physical process, it is generally applicable to less polar organic compounds with molecular weights lower than 1000 Da, which can be vaporised without dissociation. The vaporised sample is bombarded by electrons having sufficient energy to cause ionisation. The EI mass spectra obtained are relatively highly reproducible but it is a much harder ionisation method than others.

Chemical ionisation is a much more controllable method of ionisation than EI. It involves reaction of the neutral analyte with an ion generated by a high pressure EI process. A variety of types of molecular ion can be formed. The CI method is more versatile because it depends on chemical reactions that yield particular products and deposit a controlled amount of energy into them. This process allows selective ionisation of particular compounds present in a mixture.

Spray ionisation procedures produce a mist of fine droplets that are then dried to yield isolated gas phase ions of intact molecules and this allows direct examination of samples in aqueous or organic solutions. This property facilitates the coupling of LC with mass spectrometers. Among SI procedures, Electron spray ionisation (ESI) procedure is the most commonly used. The process relies on sufficient energy being provided to the charged droplets formed from solution which then causes them to desolvate and subdivide to yield, ultimately, single ionised molecules. Due to the extremely high ionisation efficiency, ESI has very high sensitivity. The low detection limits go down to attomole range.

Unlike Electron ionisation and Chemical ionisation, Desorption ionisation methods are not limited to volatile samples and allow mass spectra to be recorded for samples in the condensed phase. The delivery of intact molecules to form condensed phase samples in the gas phase as ions is the objective and the great success of DI. Energy is absorbed by the matrix in a localised region on the surface of the sample. Due to the very rapid heating involved, the analyte acquires translational energy without being internally excited to a corresponding extent. In MALDI, this translational excitation occurs by the expansion of the vaporized matrix and this releases the analyte from the condensed phase into the vacuum. When the analyte is precharged, such as a salt, the intact cation is simply transferred as an ion from the solid to the vapor state on laser irradiation of the matrix. Alternatively, the energy of the laser can cause the neutral analyte to be ionised by an ion-molecule reaction.

MALDI is the newest of the DI methods and is an extremely sensitive technique that gives predominantly singly charged ions. Among various mass spectrometer systems Time of Flight (TOF) is most commonly used mass analyser for MALDI. Detailed discussion on MALDI-TOF MS can be seen in Chapter 5.

1.4.3 The Time of Flight system

When the Time of Flight system is applied, ions are accelerated in an electric field and fly down to a detector. With the lighter ions flying faster and so reaching the detector before the heavier ions. By measuring the time of flight of an ion from its formation to its detection and using appropriate calibration, we get a measure of its *m/z*. The intensities and flight times of each ion pack are registered and converted into a mass spectrum.

Not all of the ions start off from the target with the same velocity, and this variation can lead to limitations in resolution and mass accuracy. To overcome these limitations various technologies were developed including the reflectron mode to compensate for the initial velocity distribution of the ions and so improving resolution.

Any ion of mass *m* when accelerated by a potential V_{acc} volts, gains a velocity of *v*, has a kinetic energy given by

$$eV_{acc} = \frac{1}{2}mv^2 \qquad \textbf{(1-5)}$$

Where *e* is the electronic charge

So, for a mass *m*, its velocity is given by:-

$$v = \sqrt{\frac{2eV_{acc}}{m}} \qquad \textbf{(1-6)}$$

Therefore, it can be seen that the velocity of an ion accelerated through a fixed potential is inversely proportional to the square root of its mass. Consequently, the time of flight of an ion over a fixed distance is *proportional* to the square root of its mass. This leads to a calibration law for time of flight mass spectrometers of the form:

$$\sqrt{m} = At + B \qquad \textbf{(1-7)}$$

where A and B are instrumental constants. A calibration curve for time to mass conversion looks like the curve shown below in figure 1-2.

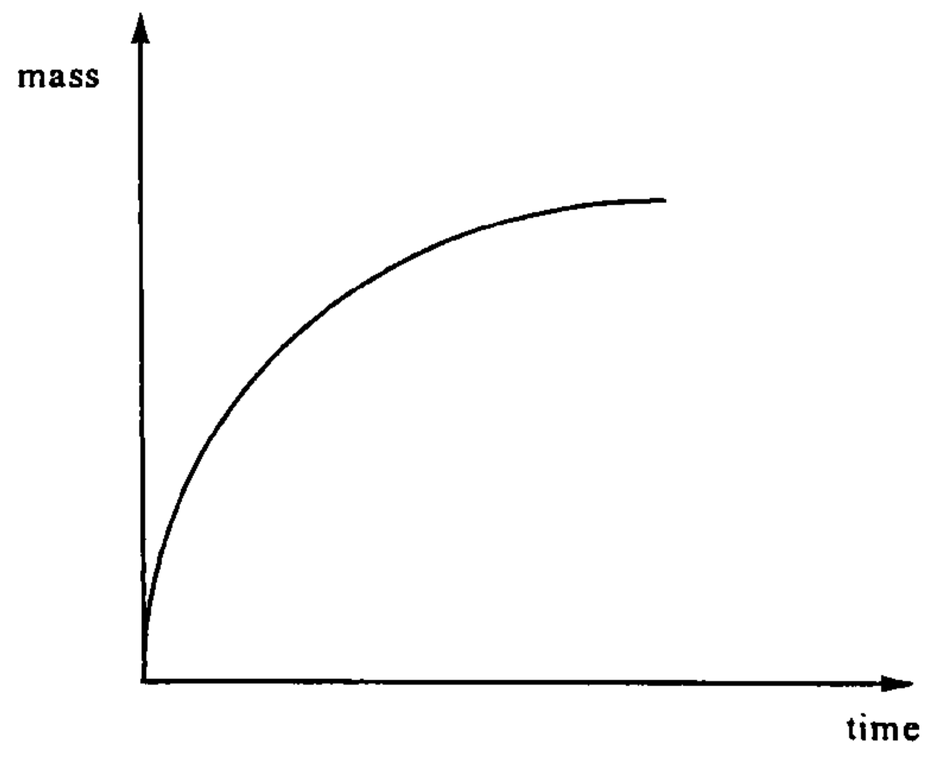


Figure 1-2: Parabolic time to mass characteristic for TOF instruments

Chapter 2. Experiment and Characterisation

2.1 Materials

2.1.1 Materials for the synthesis of iBVE-HCl

iBVE was distilled twice over CaH_2. Hexane (99+%, BDH) was distilled twice over CaH_2 before use. Charcoal was dried at 120°C over three days. Silicon gel was dried in 100 °C oven for more than 24 hours. Sodium chloride (99%) and concentrated sulfuric acid (98%) were used as received.

2.1.2 Materials for synthesising silyl enol ether 2 and 3

Redistilled chlorotrimethylsilane (CTMS, 99+%, Aldrich) was used as received. Triethylamine (TEA, 99%, BDH) was distilled over CaH_2. Anhydrous pentane (99+%, Aldrich) was used as received. N,N-dimethylformamide (DMF, 99%, BDH) was distilled over CaH_2 under the vacuum of 6~8 mmHg. 4-methoxyacetophenone (MAP, 99%, Aldrich) was dried under vacuum over night. Potassium iodide (99+%, Aldrich) was dried at 120°C overnight. 3,3-dimethyl-buta-2-non (98%, Aldrich) was distilled over CaH_2. Anhydrous THF was obtained by refluxing and distilling under dry argon over sodium (40wt.% dispersion in light oil) and benzophenone. Pentane (98%, Aldrich) was distilled and stored over 4A molecular sieves.

2.1.3 $Yb(OTf)_3$ catalysed polymerisation of iBVE

Isobutyl vinyl ether (iBVE, 99%, Aldrich) was washed with NaOH aqueous solution three times and then distilled water three times, dried with $MgSO_4$ and distilled over CaH_2 twice. Dichloromethane (DCM, 99%, BDH) was distilled over CaH_2 twice and stored over A4 molecular sieves. Ytterbium triflate, ($Yb(OTf)_3$, 99.99% , Aldrich) was dried at 100 °C overnight and dissolved in anhydrous tetrahydrofuran (THF) to make a solution of 0.1 mol L^{-1} before use. Ammonia (2.0 mol L^{-1} in methyl alcohol, Aldrich) was used as received. Trimethyl-(1-phenyl-vinyloxy)-silane, , silyl enol ether 1 (98%, Aldrich), was used as received. $ZnCl_2$ (1.0 mol L^{-1} in diethyl ether from Aldrich) was used as received. $SnBr_4$ were dried under

vacuum oven over night and dissolved in freshly distilled DCM to make 0.5 mol L^{-1} solution before use.

2.1.4 $SnCl_4$ catalysed polymerisation of vinyl ethers

Isobutyl vinyl ether (iBVE, 99%, Aldrich) and ethyl vinyl ether (EVE, 99% from Aldrich) were washed with 10% NaOH aqueous solution three times and then with water three times, dried with $MgSO_4$ and then distilled over CaH_2 twice. Methyl vinyl ether (99%, Aldrich) was used as received. Dichloromethane (DCM, 99%, BDH) was refluxed over CaH_2 for 4 hours and freshly distilled before use. $SnCl_4$ (1.0 mol L^{-1} in DCM from Aldrich) was used as received. Ammonia solution (2.0 mol L^{-1} in methyl alcohol, Aldrich) was used as received. Tetra-*n*-butylammonium chloride (99%, Aldrich) was dried under vacuum over night before use. Trimethyl-(1-phenyl-vinyloxy)-silane, silyl enol ether 1 was used as received. 1-trimethylsiloxy-cyclohex-1-ene, silyl enol ether 6 (99% from Aldrich) was used as received. (98%, from Aldrich) was used as received. Silyl enol ether 2 and 3, trimethyl-(1-4-methoxyphenyl-vinyloxy)-silane and 2,2-Dimethyl-1-(methylene-propoxy)-trimethyl-silane were synthesised and were used as end-capping agents. (1-Methoxy-2-methyl-propenyloxy)-trimethyl-silane, silyl enol ether 4, (99% from Lancaster Synthesis) was used as received. 3-Methoxy-1-methylene-allyloxy)-trimethyl-silane, silyl enol ether 5, (99% from Lancaster Synthesis) and (cyclohex-1-enyloxy)-trimethyl-silane, silyl enol ether 6 (99%, Aldrich) were used as received.

2.2 Synthesis and polymerisation method

2.2.1 Synthesis of 1-(1-chloro-ethoxy)-2-methyl-propane

1-(1-chloro-ethoxy)-2-methyl-propane was synthesised by bubbling dry HCl gas through the solution of iBVE in n-hexane at 0°C for 60 minutes under vigorous stir. The HCl gas was produced by dripping concentrated H_2SO_4 onto NaCl powder. The produced HCl gas was dried by passing through concentrated H_2SO_4, then the dried charcoal and finally dried silica gel. The unreacted HCl gas was removed by bubbling dry nitrogen through the vessel at 0°C for 180min. Titration of the chlorine ion using the Volhard method quantitatively showed the formation of the initiator. For characterisation of this compound see appendix A.

2.2.2 Synthesis of trimethyl-(1-4-methoxyphenyl-vinyloxy)-silane (SEE 2)

KI (0.1mol, 16.6 g) was mixed with MAP (0.2mol, 30 grams) in a three-neck round bottom flask under dry nitrogen. Dried DMF (100ml) was added via a syringe followed by dry pentane (40 ml). TEA (0.3 mol, 42ml) was then added via a syringe at room temperature. Finally, CTMS (0.22 mol, 27.88 ml) was slowly added via a syringe. The reactant mixture was then stirred under dry nitrogen for 12 hours at room temperature. The reaction mixture was worked up by partition between pentane and cold aqueous sodium hydrocarbonate. The aqueous layer was washed by cold pentane three times. The combined pentane was washed by cold distilled water twice followed by drying over $MgSO_4$ overnight in a freezer. The pentane was removed to give silyl enol ether 2 [Lin, 1997]. The resultant silyl enol ether 2 was analysed by NMR and GC-MS as attached in appendix A and the elemental analysis result is listed below.

Bpt: 90°C/0.15mmHg;

Elemental analysis: Theoretical: C%=64.82%, H%=8.16%, N%=0.00%

Experimental: C%=64.84%, H%=8.13%, N%=0.00%

2.2.3 Synthesis of 2,2-dimethyl-1-(methylene-propoxy)-trimethyl-silane (SEE 3)

The same procedure [Lin, 1997] as synthesising silyl enol ether 2 was applied except that the ketone substrate was 3,3-dimethyl butan-2-one.

Bpt: 36-48°C/20mmHg

NMR and GC-MS analysis are attached in appendix A.

2.2.4 $Yb(OTf)_3$ catalysed polymerisation of isobutyl vinyl ether

Polymerisation of iBVE was carried out at 0°C, –16°C, –30°C and –78°C under dry nitrogen in a three-neck round-bottom flask. The polymerisation was initiated by the addition of a solution of $Yb(OTf)_3$ to a cold solution containing iBVE, initiator and silyl enol ether (either 1, 2 or 3). Generally the polymerisation was run for 8 hours except where otherwise indicated and was terminated with methanolic ammonia. The product oligomer solution was washed with 1mol L^{-1} HCl aqueous solution twice, 1mol L^{-1} NaOH aqueous solution twice and then with distilled water twice. After removal of the solvent the oligomer was placed in a vacuum oven overnight.

2.2.5 $SnCl_4$ catalysed polymerisation of vinyl ethers

Polymerisation of iBVE and EVE were carried out at 21°C, 0°C, -15°C, and -78°C under dry nitrogen in a cooling bath carrousel. Dry nitrogen was produced by passing nitrogen through a drying column filled with indicated Drierite. The polymerisation was initiated by the addition of a solution of $SnCl_4$ or $SnCl_4$ with *n*-Bu_4NCl (prechilled when the polymerisation temperature is -78°C) to the cold solution containing iBVE, initiator and silyl enol ether. The polymerisations ran from 5 minutes to 1 hour and were terminated by the addition of a solution of ammonia in methanol. The product oligomer solution was washed with 1mol L^{-1} HCl aqueous solution twice and 1mol L^{-1} aqueous NaOH solution twice and then distilled water twice. The solvent was removed to give the product polymer.

2.2.6 Polymerisation of MVE

OMVE were synthesised using a suba-seal sealed 50ml round bottom flask with DCM at -78°C under dry nitrogen. An airtight syringe was connected through a T-glass tube to the MVE gas cylinder and the reaction flask. To get the MVE into the reaction flask, the connection to the flask was turned off and the connection to the cylinder was turned on, then the MVE cylinder was turned on and the gaseous MVE was released from the cylinder to fill the syringe to 100ml, then the connection to cylinder was turned off and the connection to the reaction flask was turned on, the MVE gas automatically flowed and condensed into the cold flask through tube and needle. The amount of MVE was calculated according to the volume of the gas and the atmosphere pressure.

The initiator and silyl enol ether were then induced into the system via syringes. Finally the cold blend solution of $SnCl_4$ and *n*-Bu_4NCl was added to initiate the polymerisation and the polymerisation which lasted 45 minutes and was terminated with ammonia/methanol. The resultant solution was washed with warm water three times and then the solvent was evaporated to give the polymer.

2.3 Organic and polymer characterisation

2.3.1 SEC characterisation

SEC was carried out with a 3×30 cm high molecular weight Styragel™ 5 mm mixed gel columns (Polymer Labs.) at room temperature. The eluent was THF at a flow rate of 1.0 $cm^3 min^{-1}$ The calibration was carried out using Polystyrene standards. Combined RI and UV detection was used. OiBVE SEC fractions were collected using a Gilson FC 205 fraction collector, under the same SEC conditions.

2.3.2 NMR analysis

For chapter 3's oligomer samples ^{13}C and ^{1}H NMR spectra were obtained on a JEOL GSX 400 spectrometer using deuterated chloroform, or a Varian Mercury 200 NMR spectrometer at room temperature using deuterated chloroform. TMS was used as the internal standard. For chapter 4's oligomer samples, ^{13}C and ^{1}H NMR spectra were obtained on a Bruker AC250 and a AMX2-400 spectrometer using deuterated chloroform at room temperature. Chloroform was used as internal standard. C-H correlation NMR spectra were obtained on AMX2-400 spectrometer using deuterated chloroform at room temperature.

2.3.3 MALDI-TOF MS analysis

Equipment

MALDI-TOF spectra were obtained using TofSpec-E instrument from Micromass, equipped with co-axial geometry with a single stage reflectron with 1.5m flight tube, and 337-nm nitrogen UV laser with a pulse width of 4ns and each pulse had an energy of 180 microjoules. Experiments were carried out under reflectron mode at an accelerating potential of 20kV by a three stage source. In reflectron mode the ions are reflected by a homogeneous electric field produced by the reflectron and detected by the annular microchannel plate detector.

Sample preparation

Polymer samples were dissolved in THF (30mg/ml), DHB or dithranol were also dissolved in THF (25mg/ml), sodium iodide was dissolved in THF (3 mg/ml).

10μl of the polymer solution, 10 μl of matrix solution and 10 μl of dopants solution were mixed together in the 0.5 ml eppendorf tube to make a final concentration of 10/1/8.5 mg/ml of polymer/dopant/matrix solution.

1 μl, 2 μl or 3 μl of the mixed sample solution was applied on the target plate. The target plate was allowed to dry fully before being loaded into the MALDI-TOF mass spectrometer.

Calibration

Each standard peptide was dissolved in 0.1% trifluoroacetic acid (TFA) aqueous solution (1mg/ml), stored in sealed amber sample tube in freezer and thawed as required. Matrix solution was prepared by dissolving 10 mg of sinapinic acid in 1 ml 60% of 0.1% TFA aqueous solution and 40% acetonitrile. Due to the variable quality of this matrix the Sinapinic acid was recrystallised from a MeOH/pentane mixture [Turner, 2000].

External calibration was applied to each sample plate. Bradykinin (M_w=1060.2), Angiotensin (M_w=1296.5), Substance P (M_w=1347.6), Renin (M_w=1759.0), ACTH (M_w=2465.7), and Insulin (M_w=5733.5) were used as calibration standards. At least 100 shots were combined to produce each spectrum. Calibrated combined spectra were preferred to examine the detailed polymer ion spectra. Calibration solution was prepared by mixing of 3 μl Bradykinin solution, 2 μl Angiotensin solution, 4 μl Insulin solution, 1 μl Substance P solution, 1μl ACTH solution, 150 μl 0.1% TFA/water solution and 160 μl sinapinic acid in 40:60 acetonitrile: water solution.

Combination of SEC and MALDI-TOF MS

SEC fractionation was performed by the connection of 3×30cm high molecular weight Styragel™ 5 mm mixed gel columns (Polymer Labs.) with Gilson FC 205 fraction collector. After the polymer sample had flowed through the SEC column and had been separated by molecule size, it was collected at the fraction collector. 12 fractions were collected from 20 to 32 minutes elution time. Each fraction contains one minute of solvent or solvent/polymer flow. The resultant SEC fraction has the approximate polymer concentration of about 0.2mg/ml.

The collected SEC fractions were left for evaporating of solvent to condense to 10 times higher concentration, to give about 2mg/ml solution in THF. This was used as polymer solution to prepare the MALDI-TOF MS samples. THF was applied as the solvent for SEC and MALDI sample preparation. The final MALDI-TOF MS sample contains about 1mg/ml OiBVE and 5mg/ml DHB and the clear MALDI-TOF mass spectra were produced.

2.3.4 LC-ESI-MS analysis

LC was carried out using a Micromass equipment through a Waters Steel Cartridge C-8 reverse phase (3.9×150mm, filter size 2 μm) column on Waters 2690 Separations Module. For the analysis of OMVE, 100% methanol was applied as eluent at the flow rate of 1 $cm^{-3}min^{-1}$. For OiBVE samples, a combination of 70% methanol and 30% THF were used as eluent at the flow rate of 1 $cm^{-3}min^{-1}$. The flow was split in the ratio of 5:1 prior to entry to the ESI source.

ESI-MS analysis was carried out using a Micromass LCZ Platform operating in ESI mode with a 4k Daltons mass range single quadrupole mass analyser. The optimised parameters were set at: capillary voltage 3.5 kV, cone voltage 130V, extractor voltage 4 V, desolvation temperature 300°C.

2.3.5 GC-MS and quantitative GC

GC-MS of the initiators and silyl enol ethers were obtained by AutoSystem XL GC/TurboMass system, Perkin – Elmer. The column was a Perkin Elmer Elite-5(5% phenyl)methylpolysiloxane Series Capillary Column

Quantitative GC was obtained on a Perkin Elmer 8410 Gas Chromatography using a packed column of SE 30, and Perkin-Elmer 8420 Capillary Gas Chromatograph using a capillary column of AT-1/film=5 μm/60m/-32Mmid from Alltech Capillary Column. Butyl ethyl ether (BEE) was applied as internal standard for the measurement of isobutyl vinyl ether conversion rate.

Chapter 3. $Yb(OTf)_3$ Catalysed *ab Initio* Cationic Polymerisation

3.1 The application of $Yb(OTf)_3$ as co-initiator

Lanthanides refer to the 14 elements following lanthanum in the periodic table from lanthanum (Z=57) to lutetium (Z=71). The electronic configuration of the lanthanides is [Xe]$4f^{0}$ to [Xe]$4f^{14}$. Since the $4f$ electrons of the lanthanides are relatively uninvolved in bonding, the highly electropositive elements have their prime oxidation number of +3 and overall, closely resemble one another chemically and physically [Cotton, 1988].

Ytterbium (Z=70) is the 13th element of the lanthanides with the electronic configuration of $4f^{14}6s^{2}$. The Ytterbium ion Yb^{3+}, with the electronic configuration of $4f^{13}$, has the radius of 1.01Å which means that it has a higher charge to radius ratio compared with most other lanthanides. It was reported that the acidity of lanthanide compounds increases with decreasing ionic radius [Satoh, 2000a], so that ytterbium trifluoromethanesulfonate ($Yb(OTf)_3$, $OTf=OSO_2CF_3$) has relatively strong acidity among lanthanide triflates.

Because $Yb(OTf)_3$ was reported to be a water resistant Lewis acid in cationic polymerisation of isobutyl vinyl ether [Satoh, 1997], it is possible that it may be applied in emulsion cationic polymerisation and with ultimately this in mind its use was investigated further in this research.

Lanthanide triflates were recently applied as Lewis acids to mediate emulsion cationic polymerisation of *p*-alkoxystyrenes and *p*-hydroxystyrene [Satoh, 1999a; Satoh, 2000b]. Living cationic polymerisation of *p*-methoxystyrene using lanthanide triflates as co-initiators were reviewed by Satoh et al. [Satoh, 1999b]. The lanthanides being applied include Yb, Sc, Dy, Sm, Gd and Nd. Among them $Yb(OTf)_3$ is proved to have the strongest ability to catalyse cationic polymerisation.

In the initial work $Yb(OTf)_3$ was chosen to catalyse the cationic polymerisation of isobutyl vinyl ether initiated by iBVE-HCl. Chain end modification during this polymerisation was explored. Under our conditions this initiation system gave oligomer samples with broad molecular weight distributions. The lack of further chain growth and the presence of aldehyde and alkene chain ends observed from NMR indicated a non-living polymerisation system. The results are accordance with the former report [Satoh, 1997]. The aldehyde chain ends probably come from the

intramolecular termination of the propagating chain end via elimination of 2-methylpropene and/or water capping of the carbocationic chain end.

3.2 $Yb(OTf)_3$ initiated cationic polymerisation of iBVE

3.2.1 Polymerisation process analysis

Figure 3-1 shows the monomer conversion at various times during the polymerisation of iBVE. The initial monomer concentration of the polymerisation is 0.43 mol L^{-1} and the initial monomer to initiator concentration ratio is 1000:1. At 80 minutes polymerisation time, the monomer conversion is 77%. For an ideal living polymerisation the resultant M_n at 77% monomer conversion should be 77000 g mol^{-1}, but the M_n by SEC of the polymer sample at 80 minutes is 4580 g mol^{-1}. Evidence for chain transfer in this polymerisation is shown in figure 3-2, the MALDI-TOF mass spectrum of the OiBVE sample. The ion mass of the strongest peak in figure 3-2 is 824.5 and it is best matched with alkene chain end, which comes from chain transfer reaction during polymerisation. A typical analysis of oligomer ion mass (*m/z* value) is shown below. An oligomer ion presented in MALDI-TOF mass spectrum consists of 4 parts. They are chain head group, repeat units, chain end group and an attached ion. For oligo(isobutyl vinyl ether) with sodium ionisation, the molar mass of these four parts are:

Only one α-end group was observed in this research, it is the proton,

M=1.0 Dalton,

When the oligomer chain contains 7 repeat units,

$-(iBVE)_7-$: M=7×100.1=700.7 Daltons

Several different chain ends were observed, when an alkene chain end is present,

$-CH_2=CH(iBVE)$: M=99.1Da

Ionisation via a sodium attachment,

Na^+, M =23.0 Daltons

The total molar mass of oligomer ion is:

M_{total} =1.0+700.7+99.1+23.0 = 823.8 Daltons

The large amount of chain transfer indicates a non-optimised balance of the ion pair at the carbocationic chain end, and that the co-initiator is not perfectly matched to the initiator for the living polymerisation of iBVE.

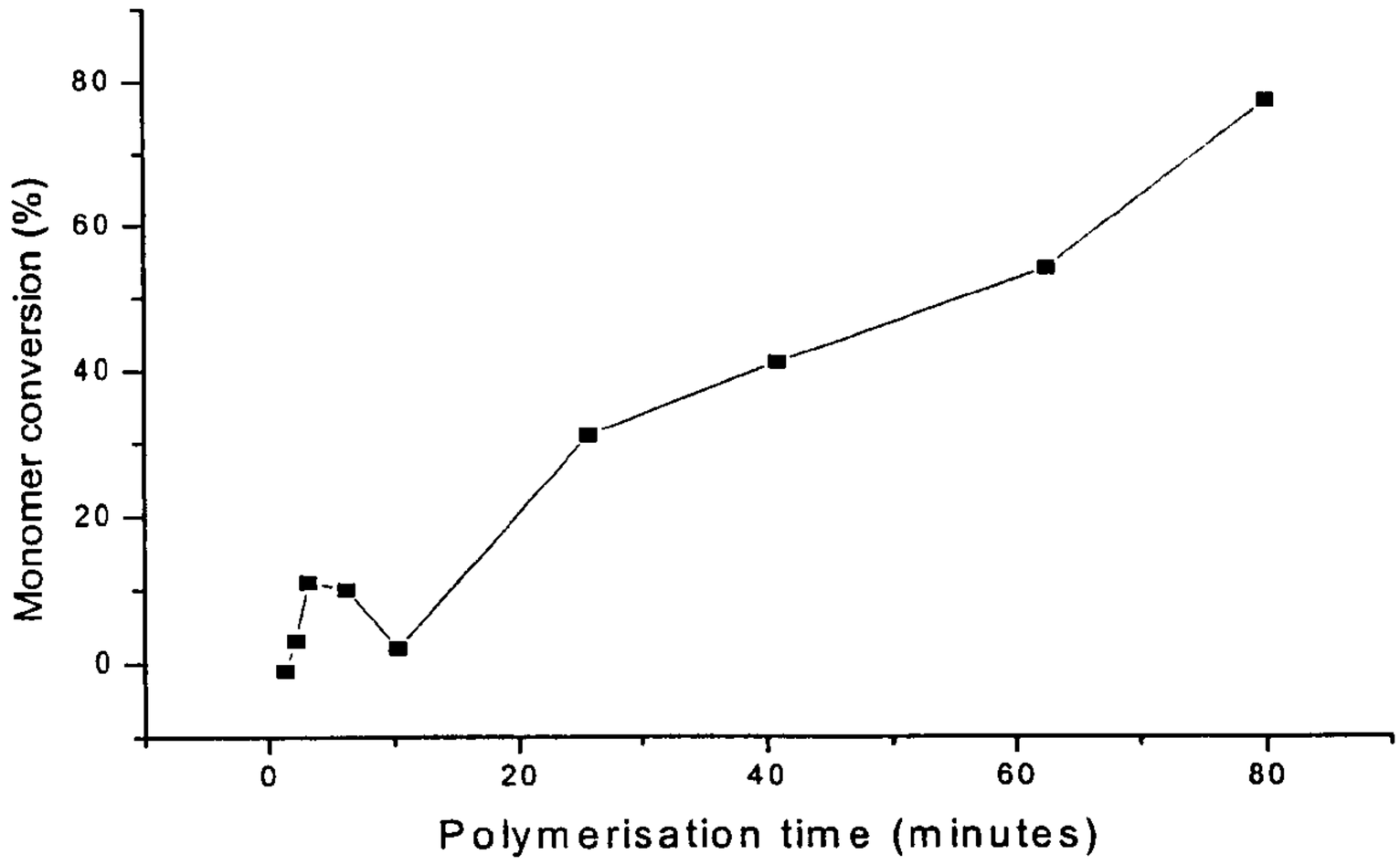


Figure 3-1: Monomer conversion at very low initiation concentration

Initial [iBVE]=0.43 mol L^{-1}, Initial [iBVE]:[iBVE-HCl]:[Yb(OTf)$_3$]=1000:1:1, polymerisation temperature: -30°C, M_n =4580, PD=2.07

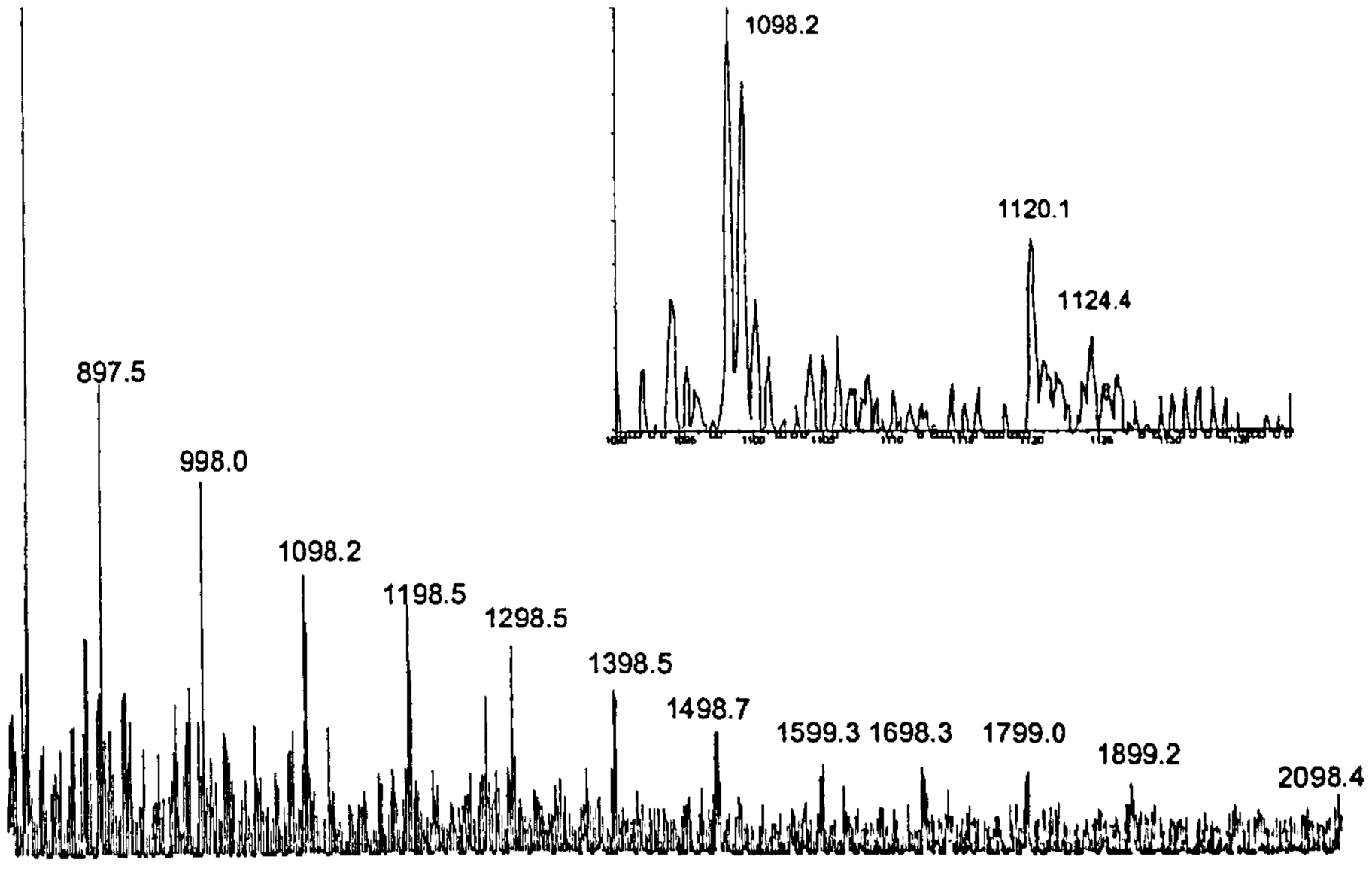


Figure 3-2: MALDI-TOF mass sepctrum of OiBVE from polymerisation process analysis

Initial [iBVE]=0.43 mol L^{-1}, Initial [iBVE]:[iBVE-HCl]:[Yb(OTf)$_3$]=1000:1:1, polymerisation temperature: -30°C, M_n =4580, PD=2.07

3.2.2 Monomer initial concentration and the additional feeding

Table 3-1 gives polymerisation data for reactions carried out with different initial monomer concentrations and data from additional sequential feeding of the monomer. The calculated theoretical degrees of polymerisation are very different from the experimental data as shown in the table. The data show that the M_n of the oligomers increases with increased initial monomer concentration. Increased initial monomer concentration should lead to increased chain initiation, chain propagation and chain transfer to monomer directly. For a living system, suppressed chain termination and chain transfer will result in a linear increase in the rate of propagation as the monomer concentration increases and thus molecular weight increase will be linearly related to the increase in monomer concentration. Therefore, the quantity M_n /[M] should be constant with changing [M]. But in table 3-1 the M_n/[M] decreases with increasing [M] and this is an additional indication of a non-living system.

However, according to the molecular weight and the monomer conversion data in the table, additional feeding of the monomer (run 4) did lead to further polymerisation. This means that 180 minutes after the initiation when the monomer of the first addition was consumed, there were living chain end left for further polymerisation.

Table 3-1: Changing of initial monomer concentration and additional feeding of monomer

run	Monomer amount (mol)	Addition of iBVE (ml)	M_n	PD	Monomer Conversion (%)	(M_n/Monomer amount) $\times 10^{-5}$	(Yield/ M_n) $\times 10^4$
1	7.68×10^{-3}	1	1400	1.60	88	1.82	4.85
2	1.54×10^{-2}	2	2340	1.69	84	1.52	5.49
3	3.84×10^{-2}	5	5310	1.51	99	1.38	7.16
4	3.84×10^{-2}	3+2	5610	1.72	84	1.69	5.07

Polymerisation conditions are the same except the initial monomer concentration. The polymerisation temperature is -30°C, the initial initiator and $Yb(OTf)_3$ concentrations are 6.3×10^{-3}mol L^{-1}. Reaction time is 180 minutes, Run 4 is the polymerisation with additional feeding of the monomer, the second feeding is 180 minutes after the initiation. The final termination is 120 minutes after the second feeding.

3.2.3 The effect of Lewis acid concentration

The analysis of the polymerisation process showed that lower Lewis acid concentration leads to slower polymerisation and higher molecular weights as expected.

Two parallel polymerisations were run under the same polymerisation conditions but with different Lewis acid concentrations. Along with polymerisation time the monomer conversions and molecular weight distributions were analysed and are shown in figure 3-3 and 3-4.

From figure 3-3 it can be seen that although the initiator concentration is very low compared with the monomer concentration, the polymerisation is still very fast. At 60 minutes polymerisation time the monomer signal totally disappeared in the GC analysis. With lower Lewis acid concentration the M_n reached 7110 g mol^{-1} at 5 minutes polymerisation time whilst with the higher Lewis acid concentration the M_n reached to 14090 g mol^{-1} at 5 minutes polymerisation time. In both polymerisations the M_n attained the highest value after 33 minutes and reduced after that time. As mentioned before this M_n reduction could be due to the formation of shorter oligomer chains after the monomer was largely consumed. $Yb(OTf)_3$ does not lead to a well-controlled cationic polymerisation. Molecular weight distributions of the polymer samples increase as the polymerisation progresses as shown in figure 3-4.

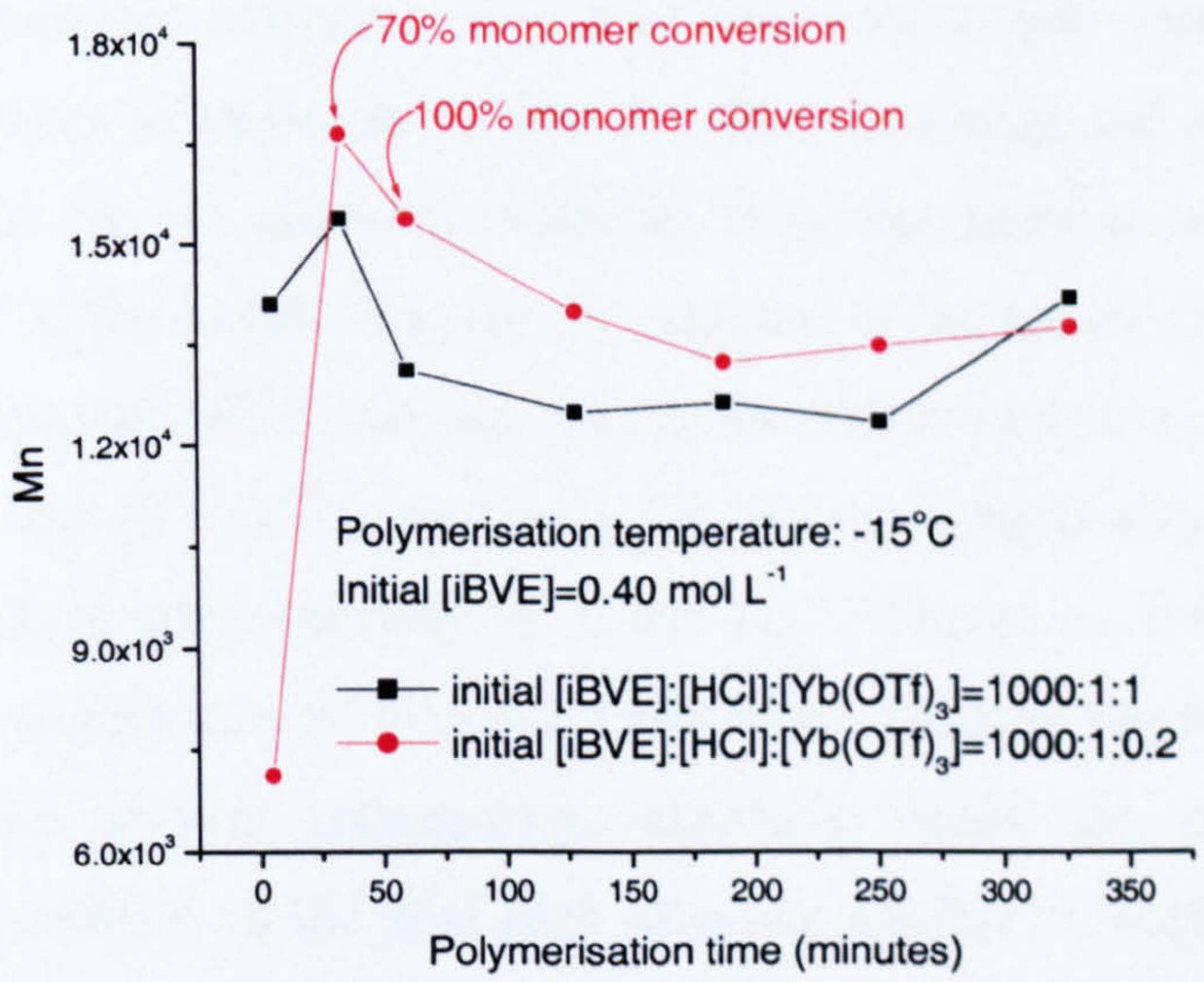


Figure 3-3: Comparison of M_n during polymerisation processes with different $Yb(OTf)_3$ concentration

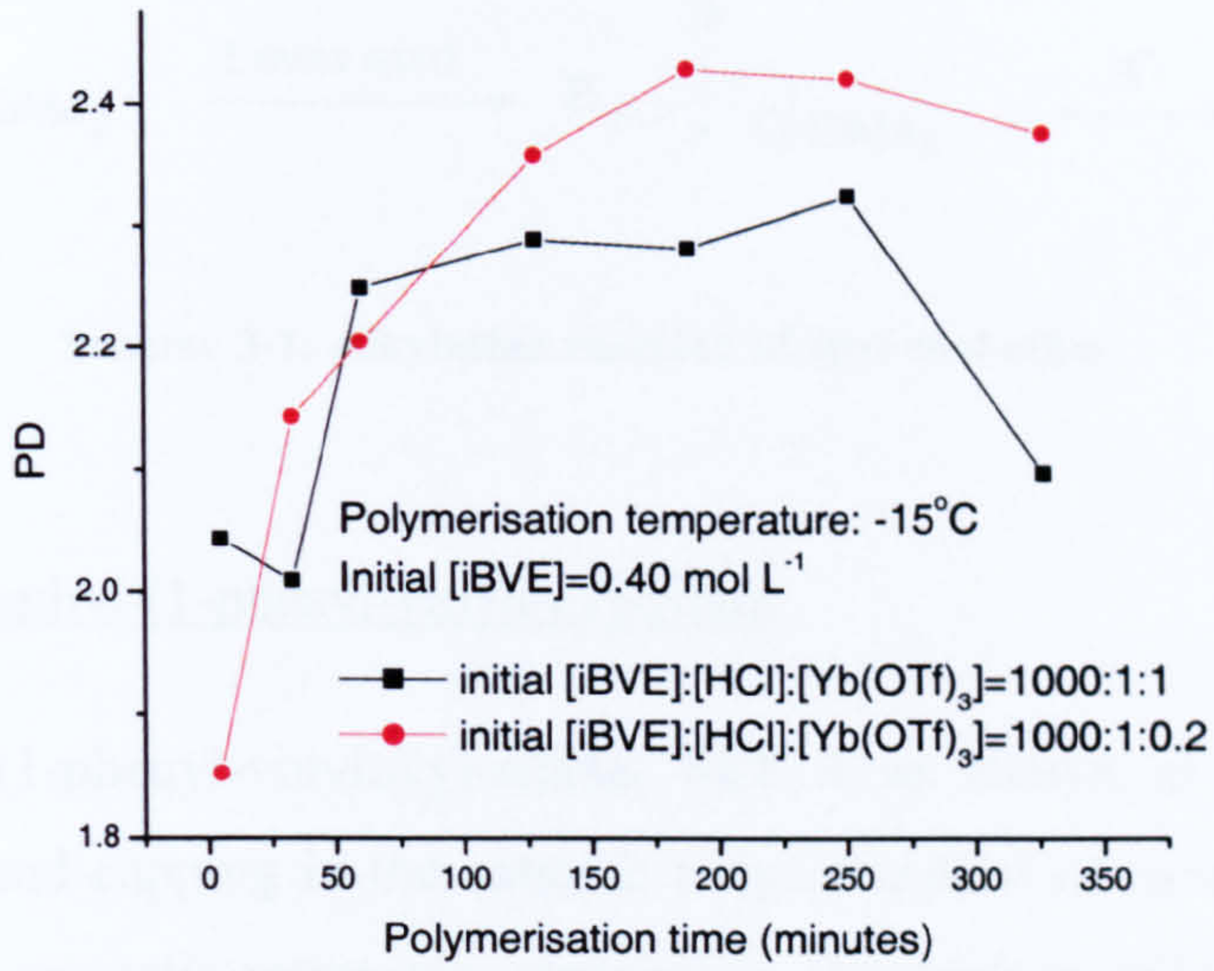
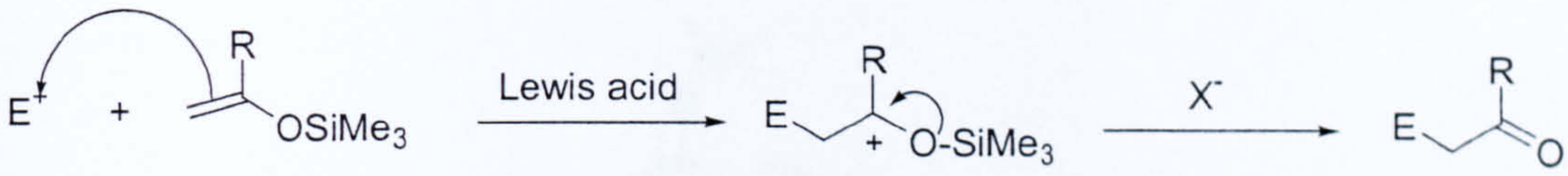


Figure 3-4: Comparison of PD during polymerisation process with different Yb(OTf)$_3$ concentration

3.3 *Ab initio* chain end functionalisation

Side reactions are clearly an issue in these reactions but the significance of these can be reduced by deliberately adding a species that can react with the chain end at a rate that can compete with these reactions. Such a reaction would also progress at a rate that was slower than the rate of propagation. This species being added to the chain end also can be used to add useful chain end functionality

As introduced in chapter 1, silyl enol ethers react with carbocations to yield ketone functionalities as shown in scheme 3-1. Rate constants and activation energies for these reactions are not generally available. However, Bartl et al.[Bartl, 1991] has shown that at 20° C the values of k_2 for the addition of the benzhydryl cation to vinyl ethers are approximately 10^8 L mol^{-1}sec^{-1} and k_2 for addition of the same cation to vinyl silyl enol ethers are 10^7 - 10^8 L mol^{-1}sec^{-1}. On the other hand alkyl substituted silyl enol ethers gave k_2 of approximately 10^9 L mol^{-1}sec^{-1}. Therefore, from this data it was considered that incorporation of vinyl silyl ethers in a cationic polymerisation of vinyl ethers should not prevent propagation occurring (since the rate constants for propagation and addition to the silyl enol ether are similar in magnitude). However, addition of the propagating cationic chain end to the vinyl silyl ethers should occur at a rate that would favourably compete with the slower termination reactions.



Scheme 3-1: Alkylation reaction of silyl enol ether

3.3.1 Use of trimethyl-(1-phenyl-vinyloxy)-silane

Trimethyl-(1-phenyl-vinyloxy)-silane, **SEE 1** as shown in figure 3-5, was firstly applied in end-capping in the cationic polymerisation of isobutyl vinyl ether. Small amounts of aromatic resonance appeared in the resultant NMR spectra of the oligomer samples. Also SEC overlay of the OiBVE samples with end-capping showed strong aromatic absorptions which are absent from the samples without end-capping, indicating the attachment of **SEE 1** to the oligomer.

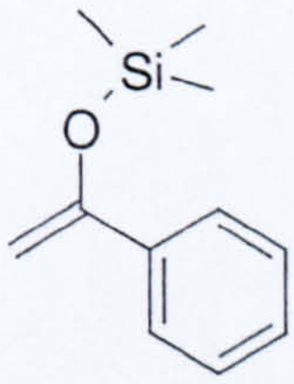


Figure 3-5: Trimethyl-(1-phenyl-vinyloxy)-silane, SEE 1

3.3.2 Use of trimethyl-(1-(4-methoxy)phenyl-vinyloxy)-silane

Because a small molecule with a strong aromatic absorption was detected in the SEC analysis of the oligomer obtained by incorporation of **SEE 1**, it was considered that the reactivity of **SEE 1** may not be high enough and the end-capping agent was left unreacted. Therefore trimethyl-(1-(4-methoxy)phenyl-vinyloxy)-silane, **SEE 2**, as shown in the figure 3-6, was synthesised. With a *para*-methoxy phenyl substitute, **SEE 2** is a stronger nucleophile than **SEE 1** and thus it has higher potential reactivity in the end-capping reaction.

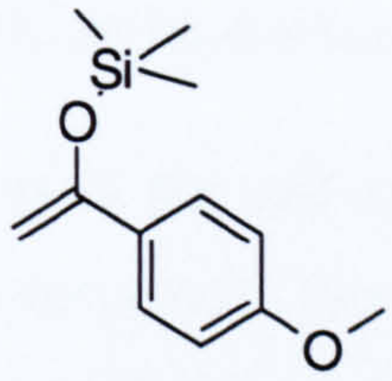


Figure 3-6: Trimethyl-(1-(4-methoxy)phenyl-vinyloxy)-silane, SEE 2

Figure 3-7 shows the SEC chromatogram of OiBVE when **SEE 2** is applied in the polymerisation. Again the strong aromatic absorption indicated the attachment of **SEE 2** to the oligomer chain. The slight delay of the UV signal could be due to short chains that present more chain ends per repeat unit and thus produce stronger aromatic absorption.

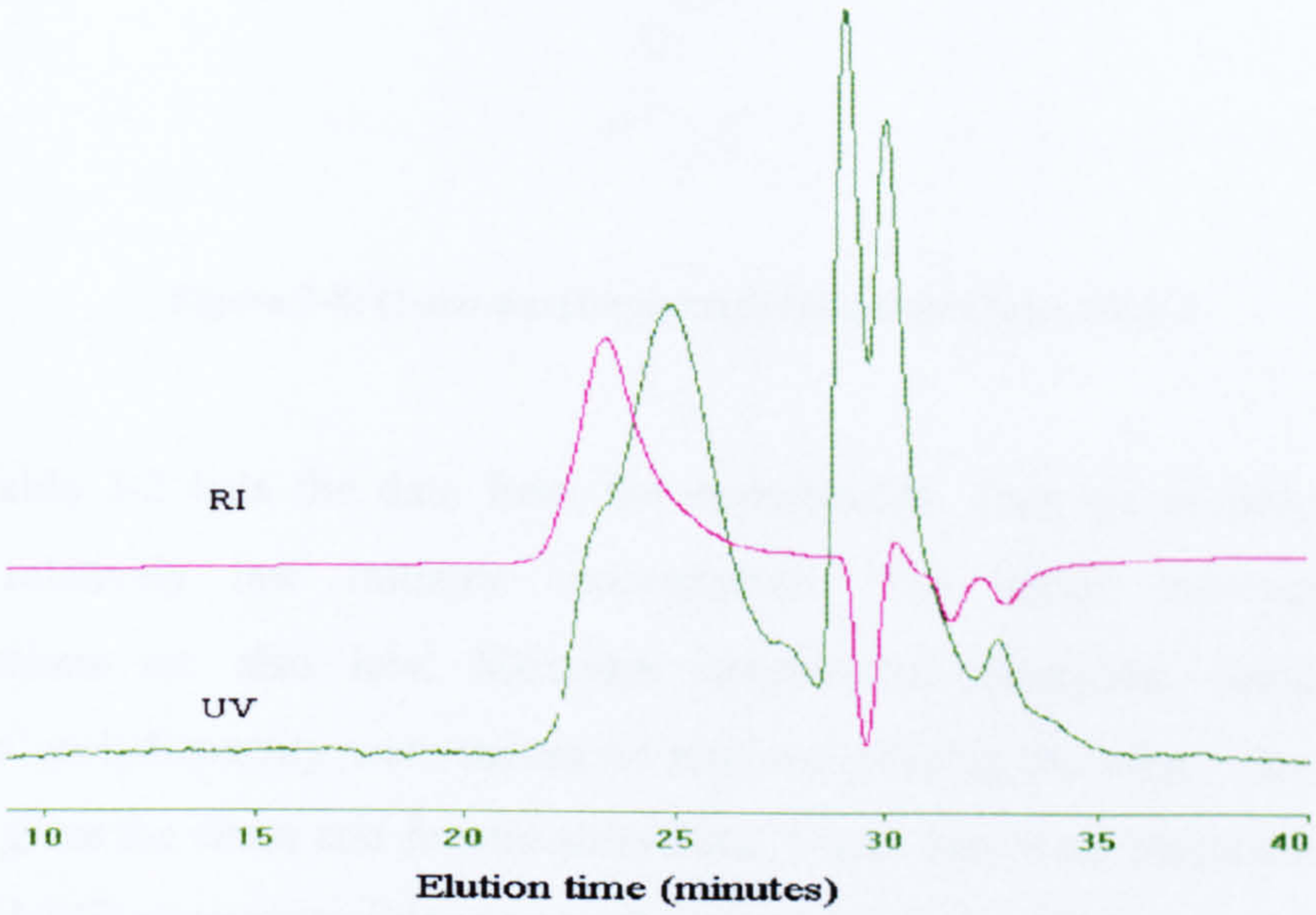


Figure 3-7: Dual SEC overlay of OiBVE sample with end-capping of SEE 2

Initial monomer concentration = 0.5 mol l^{-1}, initiation ratio: [iBVE]:[iBVE-HCl]:[Yb(OTf)$_3$]:[SEE 2]=154:1:1:1, M_n=6560, PD=1.80, Polymerisation temperature: -16°C, Polymerisation time: 100 minutes,

NMR analysis of the OiBVE end-capped by **SEE 2** also gave apparent corresponding aromatic resonances. All the experiments with *ab initio* end-capping result in high yield of oligomers. With the NMR and SEC analysis results it is safe to say that the end-capping agents being applied are attached to the oligomer chain.

3.3.3 *Ab initio* end-capping via alkylation reaction of silyl enol ethers

After the initial explorations of the end-capping with **SEE 1** and **SEE 2** in cationic polymerisation, a set of experiments were designed to investigate *ab initio* end-capping under certain initiator and silyl enol ether concentrations and different polymerisation temperatures. Oligomers obtained from control polymerisation in the absence of silyl enol ethers, were compared with the oligomers polymerised under the presence of 3 different silyl enol ethers. Apart from **SEE 1** and **SEE 2**, another silyl enol ether was designed and synthesised as a potential end-capping agent with lower reactivity. (1-*tert*-Butyl-vinyloxy)-trimethyl-silane, **SEE 3** as shown in figure 3-8, was also applied in the *ab initio* end-capping in the cationic polymerisation of isobutyl vinyl ether.

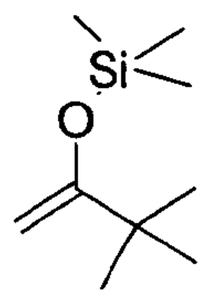


Figure 3-8: (1-*tert*-butyl-vinyloxy)-trimethyl-silane, SEE 3

Table 3-2 lists the data from the experiments. This set of polymerisations applied relatively low initiator concentration. The initial end-capping agent concentrations are also low. Monomer conversion, molecular weight and the oligomers' polydispersity were measured and are listed in the table. The column on the right gives the chain end functionality data. These data were calculated according to the ^1H NMR resonances integration when it was possible. However, because of the overlap of the α-end and ω-end resonances, chain end functionality can not be obtained for oligomers end-capped by **SEE 3** using the NMR method.

Apparently the chain end functionality was affected by temperature, highest chain end functionality was obtained at -30°C. As discussed formerly temperature affects the initiation, chain propagation, chain transfer and termination. Chain end functionality data in table 3-2 can be explained by considering that at 0°C the termination reactions occur at a rate that is faster than the end capping reactions. On the other hand at –30°C the termination reactions reduce significantly which leads to higher chain end functionality, presumably the lower end-capping rates at the low

temperature of -78°C lead to the lower chain end functionality. Thus an optimal reaction temperature for higher chain end functionality is observed.

Under the polymerisation conditions the chain end functionalities obtained are generally low. **SEE 1** and **SEE 2** gave similar chain end functionalities. A typical ^1H NMR integration analysis of OiBVE synthesised in the presence of **SEE 1** is shown in figure 3-9.

Table 3-2: Oligomer functionalisation with an initial [M]/[I] ratio of 100

Temp. °C	[M]:[I]:[L][a)]	SEE[b)]	[SEE]:[I][c)]	Additive	Conversion %	M_n g mol^{-1}	PD[d)]	Fn %
-78	100:1:1	None	0.0	BEE[e)]	90.5	4620	2.4	-
-78		1	1.0	BEE	81.6	5140	3.1	9.8
-78		2	1.0	BEE	74.7	5570	3.4	5.9
-78		3	1.0	BEE	88.0	5340	2.6	N/A
-30	100:1:1	None	0.0	BEE	92.0	10510	3.6	-
-30		1	1.0	BEE	85.3	4970	4.6	31.0
-30		2	1.0	BEE	97.7	8440	3.7	26.9
-30		3	1.0	BEE	98.2	5960	3.4	N/A
0	100:1:1	None	0.0	None	100	2880	3.9	-
0		1	1.0	BEE	96.7	4290	1.9	18.9
0		2	1.0	BEE	100	2710	3.8	18.4
0		3	1.0	None	100	2350	3.2	N/A

iBVE-HCl was the initiator, polymerisation time is 480 minutes, initial monomer concentration=0.49 mol l^{-1}

a) [M] = monomer concentration, [I] = initiator concentration; [L]= $Yb(OTf)_3$ concentration

b) SEE = reference number denoting the structure of the silyl enol ether, as it appears in the text;

c) [SEE] = silyl enol ether concentration, [I] = initiator concentration;

d) PD = polydispersity; Fn=Functionality, measured by NMR, N/A= analysis not applicable to these samples.

e) BEE is butyl ethyl ether. It was added to the polymerisation as internal standard for monomer conversion measurement on GC. The concentration of BEE is the same as the initial monomer concentration.

In figure 3-9 aromatic resonances from 7.4 ppm to 8 ppm are clearly presented. A small resonance at 2.6 ppm can also be observed. Consider that the desilylation of **SEE 1** gives acetophenone, this signal labeled as **a** in figure 3-9 is due

to the methyl group resonance of the acetophenone. The resonance labeled as **b** is due to the methyl resonance of the α-end. The ratio of the integrations of the aromatic resonance of the oligomer to the α-end methyl protons resonance was used to calculate the functionalities. A trace amount of aldehyde resonance **c** is also observed in figure 3-9.

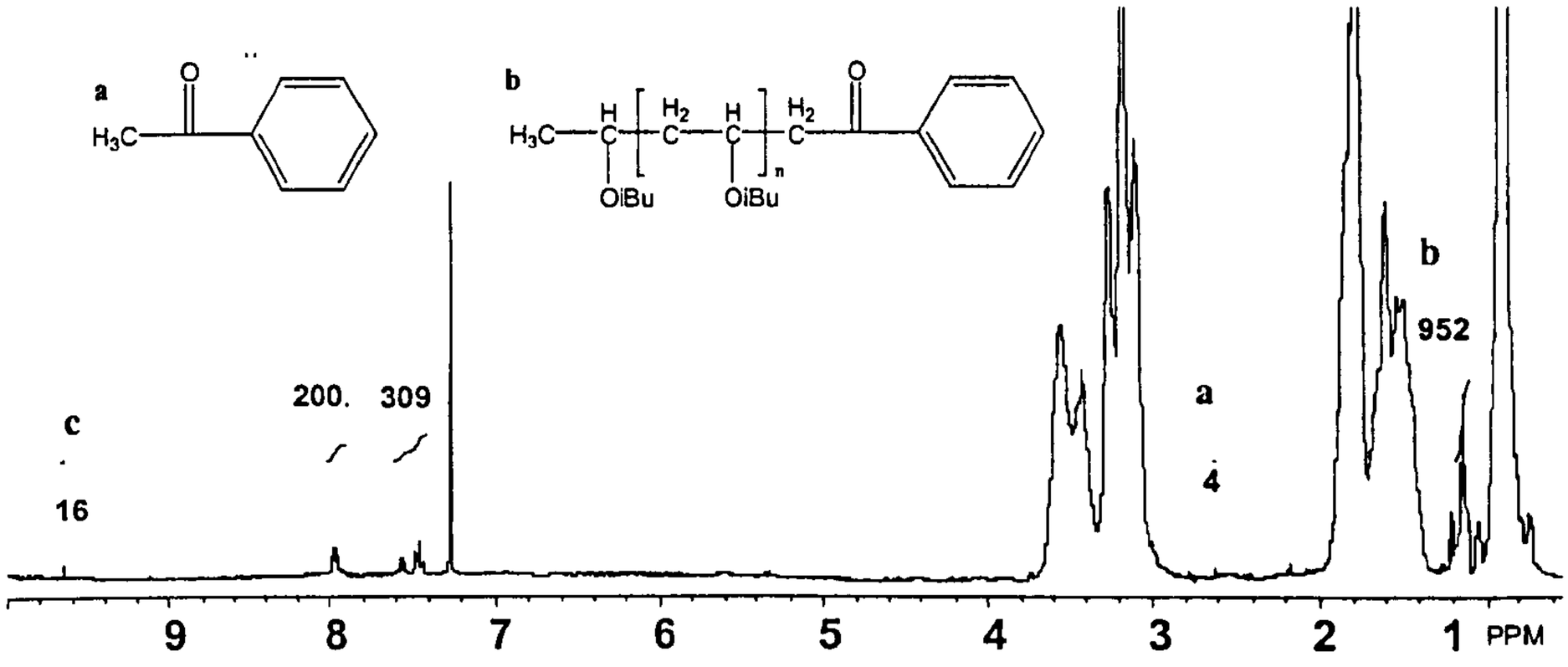


Figure 3-9: ^{1}H NMR of OiBVE partially end-capped by SEE 1

Polymerisation temperature: -30°C, initial [iBVE]:[iBVE-HCl]:[SEE 1]:[$Yb(OTf)_3$]=100:1:1:1, initial monomer concentration is 0.49 mol l^{-1}, M_n=4970, PD=4.6, Fn=31.0%

Figure 3-10 is an expanded ^{1}H NMR of the functionalised OiBVE. Again a trace resonance at 2.6 ppm is observed indicating the presence of a small amount of acetophenone in the oligomer sample. About 88% of the aromatic resonance is due to the aryl group that is attached to the oligomer chain. The other 12% is due to the resonance of acetophenone—the desilylation product of unreacted **SEE 1**. The resonance around 4.6 ppm is due to the tertiary proton of the acetal ω-end. This acetal chain end could be diisobutanol or the methanol capped chain end by the quenching procedure. Analysis of the various chain ends in detail can be largely improved through MALDI-TOF MS. Discussion on the formation of the chain ends obtained can be seen in Chapter 4.

It is clear that at these low initiator concentrations the chain end functionality obtained is low. In the next set of experiments the initiation and silyl enol ether concentration were increased to improve the end-capping rate.

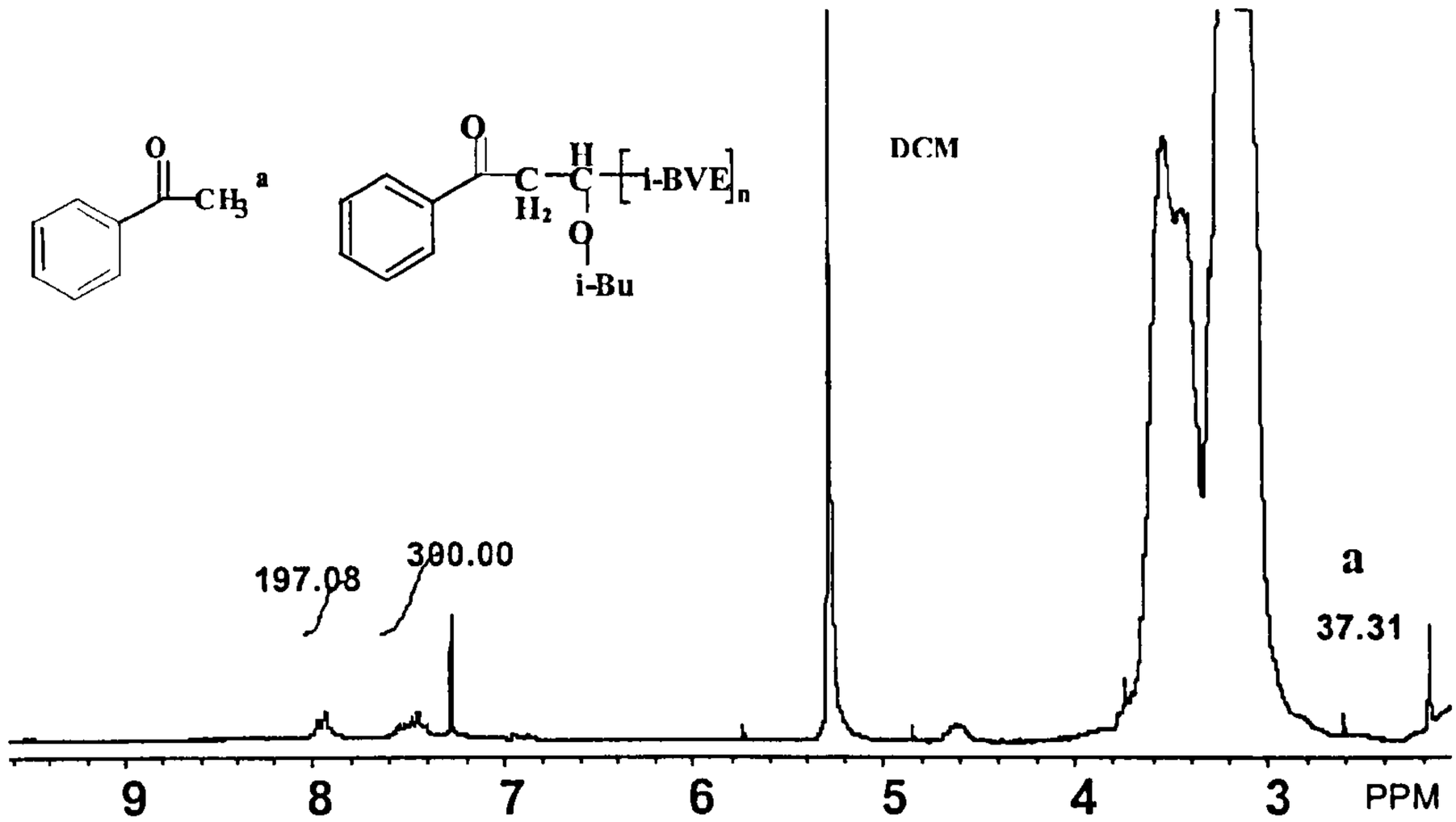


Figure 3-10: Expanded ^{1}H NMR of OiBVE end-capped by SEE 1

Polymerisation temperature: -78°C, initial [iBVE]:[iBVE-HCl]:[SEE 1]:[Yb(OTf)$_3$]=100:1:1:1, initial monomer concentration is 0.49 mol l^{-1}, M_n =5140, PD=3.1, Fn=9.8%

Table 3-3 lists the data obtained. The quantitative analyses by proton NMR indicate that these oligomers have high chain end functionality. The results clearly show that increasing the concentration of initiator and **SEE** has a large effect on chain end functionality. The addition of silyl enol ethers before initiation, at this concentration, does not seriously affect the polymerisation; that is the polymerisation remains unquenched and OiBVE can be produced in the presence of these nucleophilic agents. Using the current conditions the polymerisation of iBVE gave OiBVE of lower molecular weight and broader molecular weight distribution when it was performed in the presence of **SEE 1** and **SEE 2** than when reaction was carried out in their absence.

Again the presence of the aryl end-group was proved by NMR and the total chain end functionality was calculated according to proton NMR integration. Figure 3-11 shows the proton NMR of OiBVE end-capped by **SEE 2** and the relevant assignments of the chain ends. It can also be seen from figure 3-11 that a small amount of methoxyacetophenone, the product of desilylation of **SEE 2**, is present in the oligomer sample.

^{13}C NMR of the sample also gave the corresponding resonances of the SEE capped chain ends. Figure 3-12 is the ^{13}C NMR of OiBVE end-capped by **SEE 2**. ^{13}C

NMR of 4-methoxyacetophenone is presented in figure 3-13 with the assignments. Comparison of the two ^{13}C NMR spectra from figure 3-12 and 3-13 confirms the presence of the chain end aryl ketone group, derived from alkylation of the carbocation by **SEE**, from the aromatic resonances and the chain end methylene group adjacent to carbonyl at 45.4 ppm. The carbonyl resonance (around 196.2 ppm) is not observed in the spectrum of the oligomer nor is the methyl group resonance (26.2 ppm) from the 4-methoxyacetophenone.

Table 3-3: Oligomer functionalisation with an initial [M]/[I] ratio of 10

Temp. °C	[M]:[I]:[L][a)]	SEE[b)]	[SEE]:[I][c)]	Conversion %	M_n g mol^{-1}	PD[d)]	Fn %
-30	10:1:0.2	None	0.0	94.4	1200	3.0	-
-30		1	1.0	100	670	8.1	86.9
-30		2	1.0	90.4	1010	6.9	93.2
-30		3	1.0	100	1280	1.5	N/A
-16	10:1:0.2	None	0.0	81.7	1640	3.6	-
-16		1	1.0	98.0	1020	4.9	92.1
-16		2	1.0	88.7	820	12.9	100
-16		3	1.0	78.2	1070	1.9	N/A
0	10:1:0.2	None	0.0	98.0	1370	7.2	-
0		1	1.0	82.9	730	4.2	85.0
0		2	1.0	38.5	440	3.0	89.3
0		3	1.0	89.1	900	2.5	N/A

iBVE-HCl was the initiator, polymerisation time was 180 minutes at 0°C and 360 minutes at □16°C and □30°C. Initial monomer concentration is 0.49 mol l[1]

a): [M] = monomer concentration, [I] = initiator concentration; [L]=Lewis acid concentration

b): SEE = reference number denoting the structure of the silyl enol ether, as it appears in the text;

c): [SEE] = silyl enol ether concentration, [I] = initiator concentration;

d): PD = polydispersity; Fn=Functionality, measured by NMR, N/A= analysis not applicable to these samples.

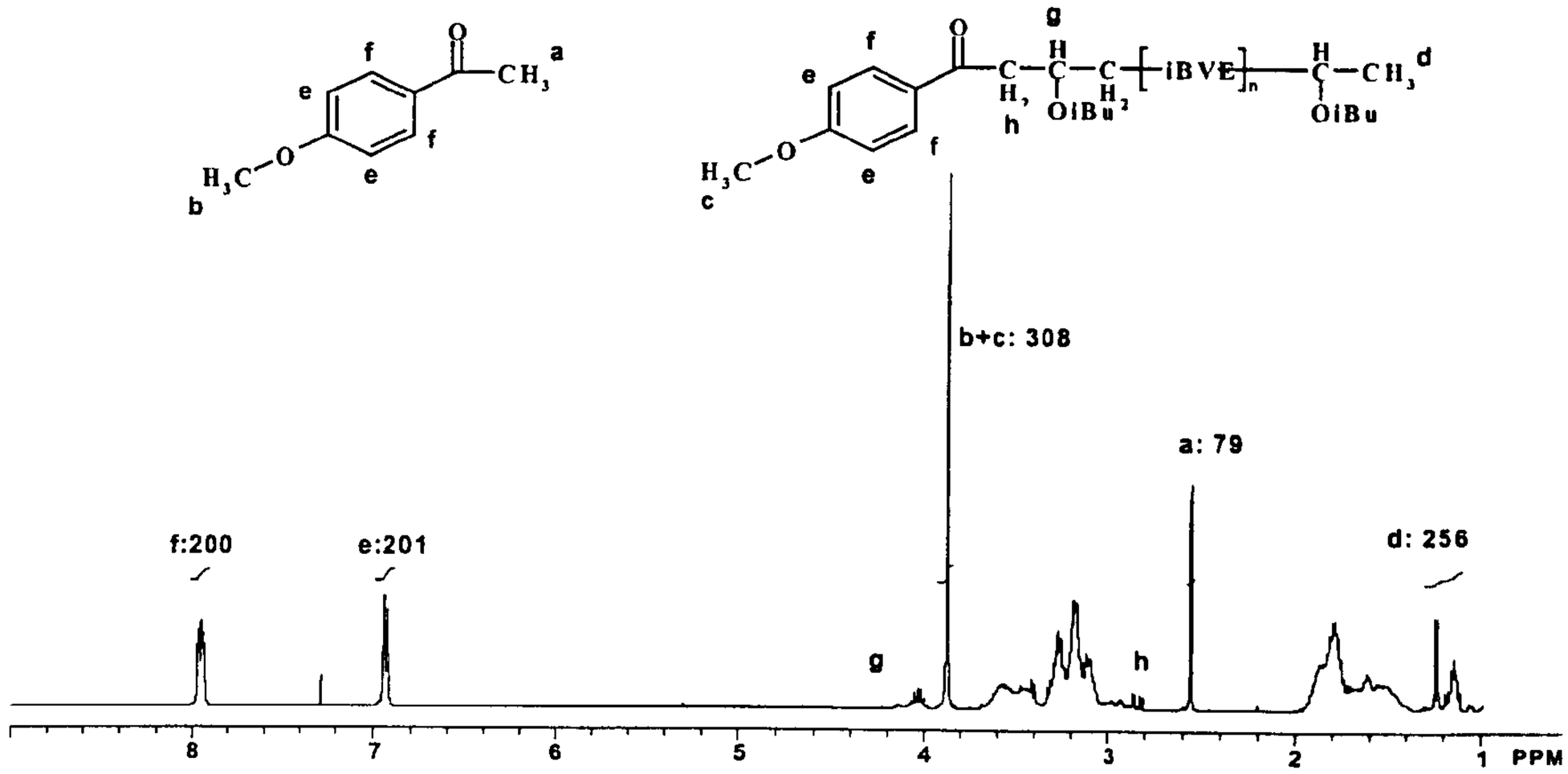


Figure 3-11: Expended ^{1}H NMR of OiBVE end-capped with SEE 2

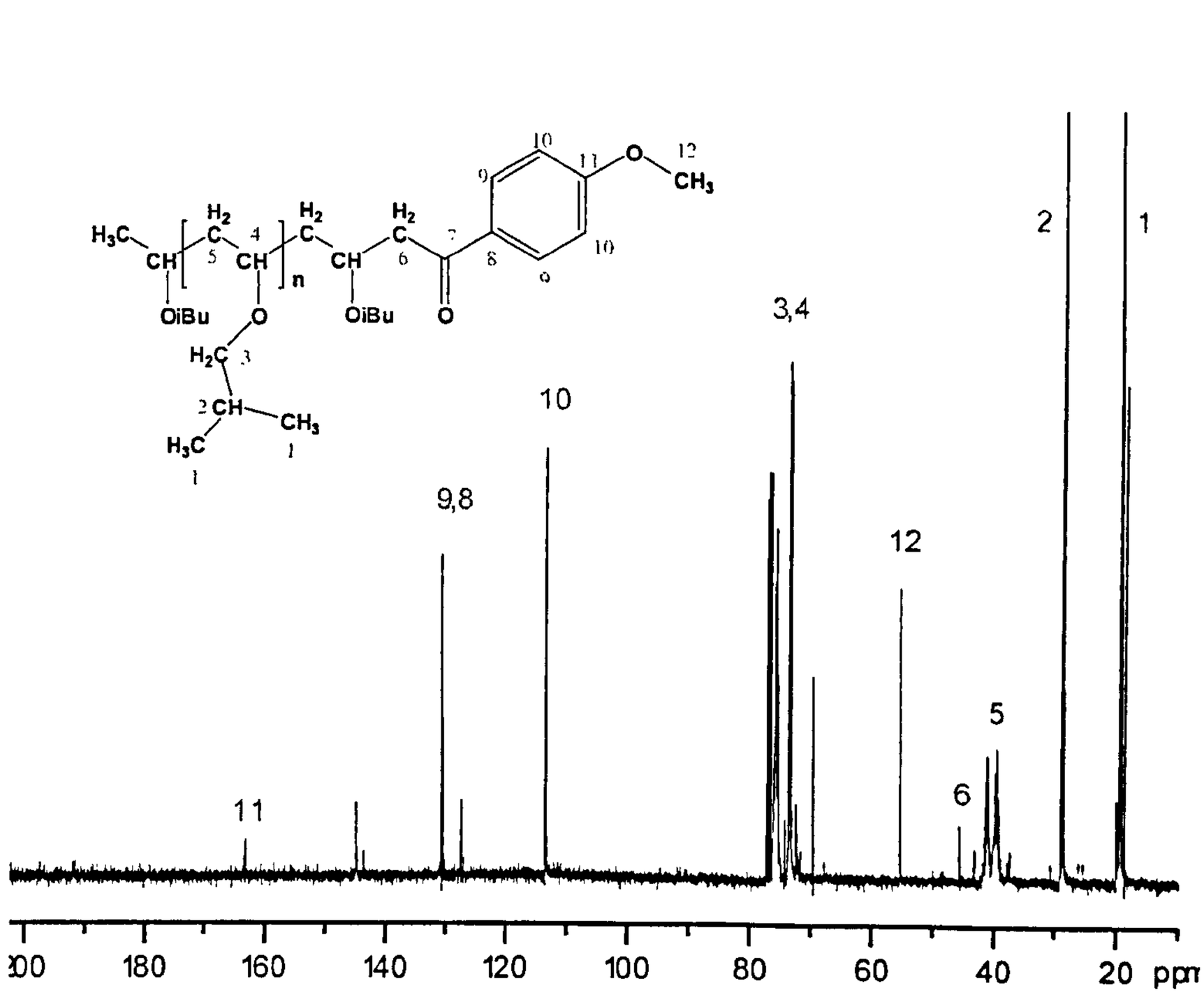


Figure 3-12: ^{13}C NMR of OiBVE end-capped by SEE 2

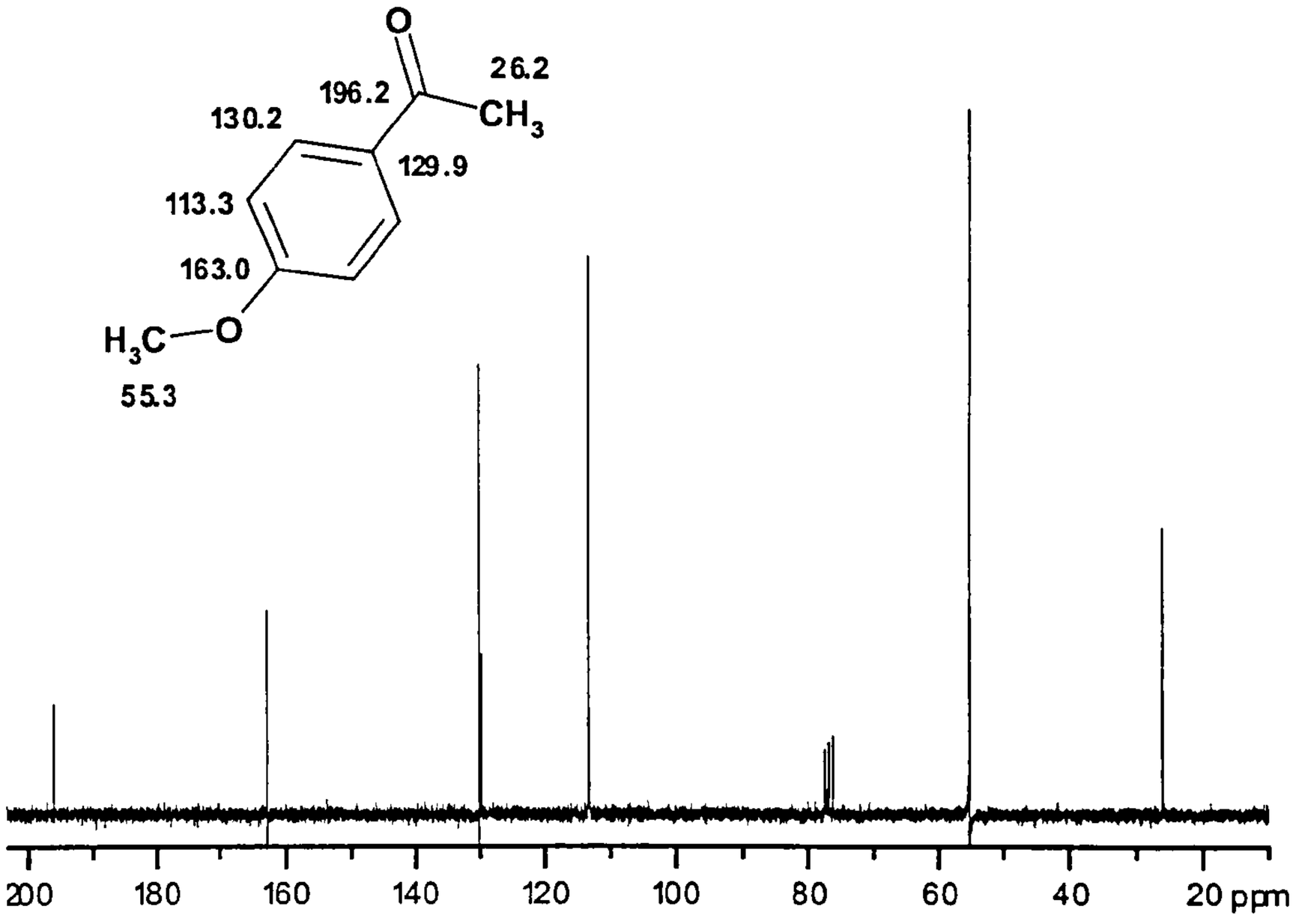


Figure 3-13: ^{13}C NMR of 4-methoxyacetophenone

3.3.4 *Ab initio* end-capping with **SEE 3**

When **SEE 3** was applied in the *ab initio* end-capping, the ^{1}H NMR of the resultant oligomer sample did not show any apparent difference from the control polymerisation except that the resonance around 1.1 ppm was enhanced. In order to examine the incorporation of **SEE 3** at the chain end the ^{1}H NMR spectrum of a reaction run in the absence of **SEE 3** was subtracted from an identical reaction run in the presence of **SEE 3**. The subtracted spectrum, shown in figure 3-14, contains mainly resonances derived from the three methyl groups that are located β to the ketone carbonyl. Also present in this subtracted spectrum is the resonance due to the methyl group α to the ketone carbonyl in the 3,3-dimethylbutan-2-one. Accurate integration of the subtracted peaks is not possible due to the small but significant errors in the subtraction process. However, it is clear from the qualitative examination of figure 3-14 that the relative ratio of α-methyl and the β-methyl proton are far from proportions expected for 3,3 dimethylbutan-2-one. So that a substantial fraction of the β-methyl groups are attached to the chain end. In ^{13}C NMR whilst the carbonyl carbon in 3,3-dimethylbutan-2-one is present at 208 ppm, a new resonance at 214

ppm was produced in the oligomer sample synthesised in the presence of **SEE 3**, indicating the formation of the ketone group from reaction of **SEE 3** with the propagating chain end.

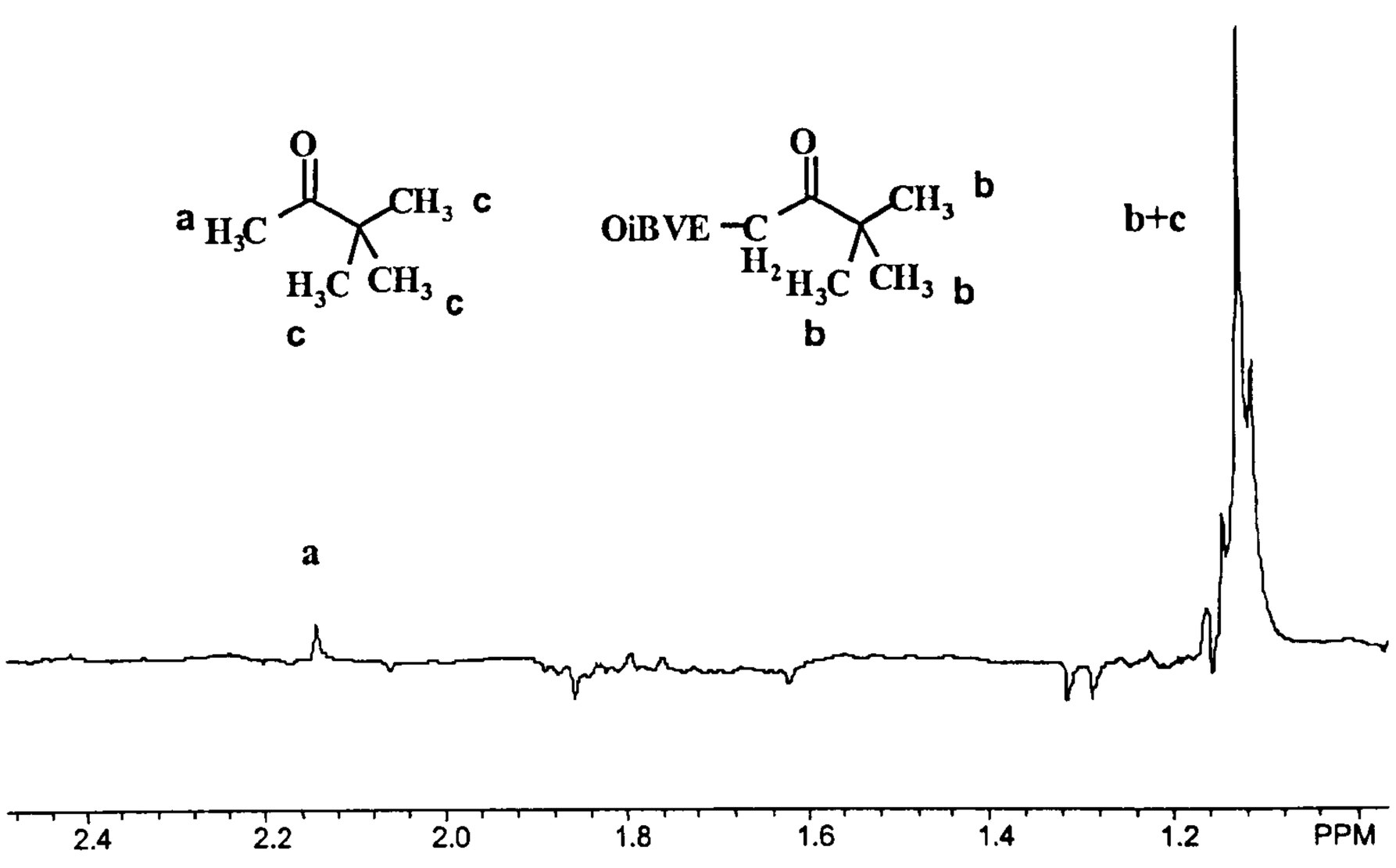


Figure 3-14: Subtracted ^1H NMR of OiBVEs from two parallel polymerisations in the presence and absence of SEE 3

From table 3-2 and 3-3 it can be seen that when **SEE 3** was applied in *ab initio* end-capping, the resultant oligomers showed narrower molecular weight distributions. Figure 3-15 shows SEC overlays of two parallel polymerisations which were run at the same time with the same polymerisation temperature and initiator concentration. One of the polymerisations was a control polymerisation carried out in the absence of any **SEE**s whilst the other was an *ab initio* polymerisation carried out in the presence of **SEE 3**. The SEC chromatograms provide clear evidence for the lower molecular weights and narrower molecular weight distributions obtained in the presence of **SEE 3** and show that **SEE 3** competes favourably with other termination and chain transfer reactions, which broaden the molecular weight distribution. The result seems to indicate a suitable end-capping rate of **SEE 3** in the current polymerisation system that lies in between the chain propagation rate and other side reactions rates.

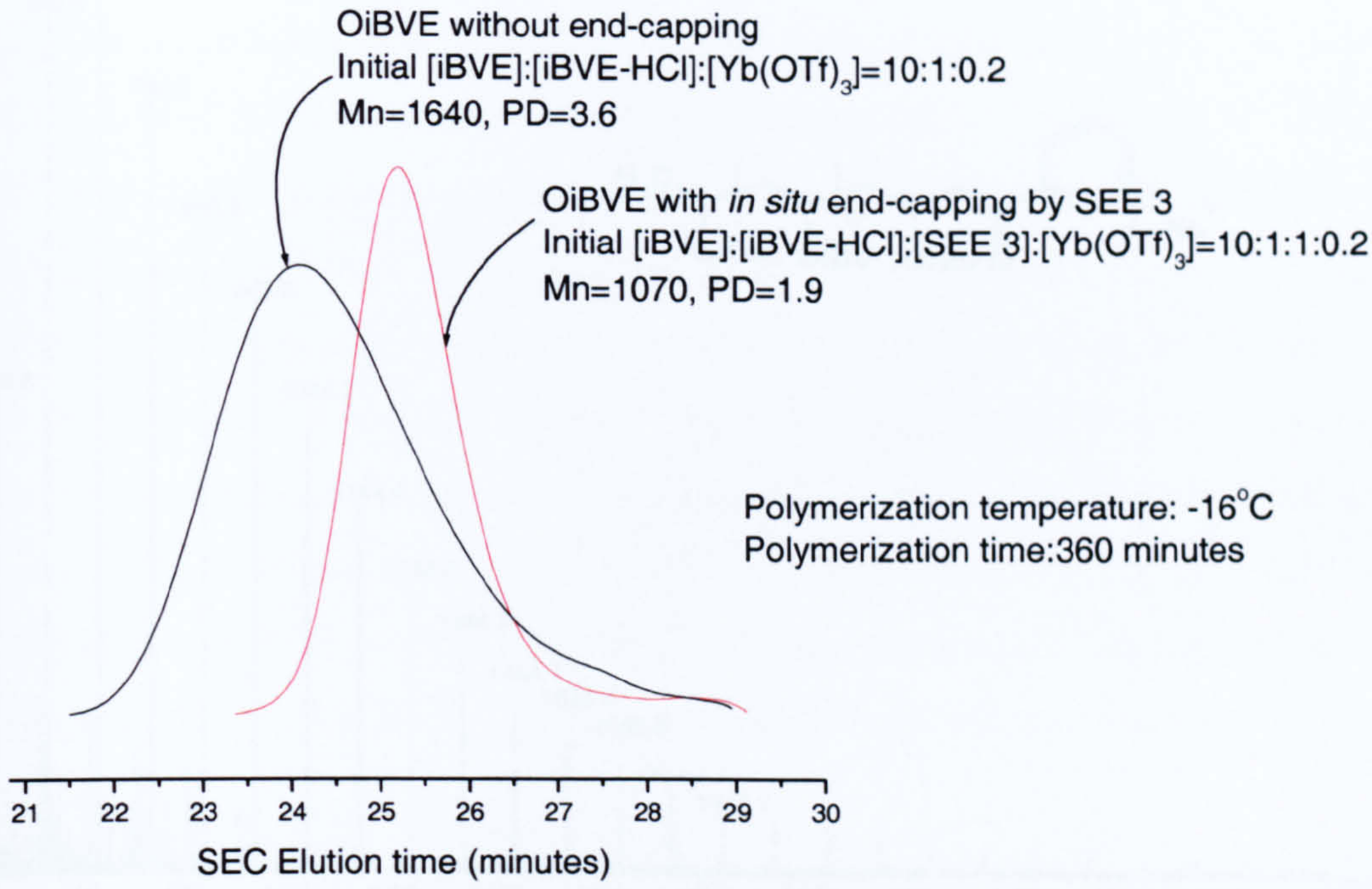


Figure 3-15: SEC overlays of the OiBVEs of *ab initio* end-capping with SEE 3 and the parallel control polymerisation

Initial [iBVE]=0.49 mol L^{-1}

3.3.5 MALDI-TOF MS analysis of OiBVE

Figures 3-16 and 3-17 show MALDI-TOF mass spectra of OiBVE produced in the presence of **SEE 1** and **SEE 2**. Each spectrum is dominated by a single series of ions indicating that copolymerisation of the silyl enol ethers, a potential complication, is not a feature of these reactions.

From these two figures it can be seen that the oligomers produced in the presence of **SEE 1** or **SEE 2** are predominately end-capped by acetyl phenone or the acetyl 4-methoxyphenone respectively. The mass peaks are separated by the repeat mass of iBVE (about 100g mol^{-1}). The residual masses indicate the presence of the acetyl phenone or acetyl 4-methoxyphenone groups plus one sodium ion.

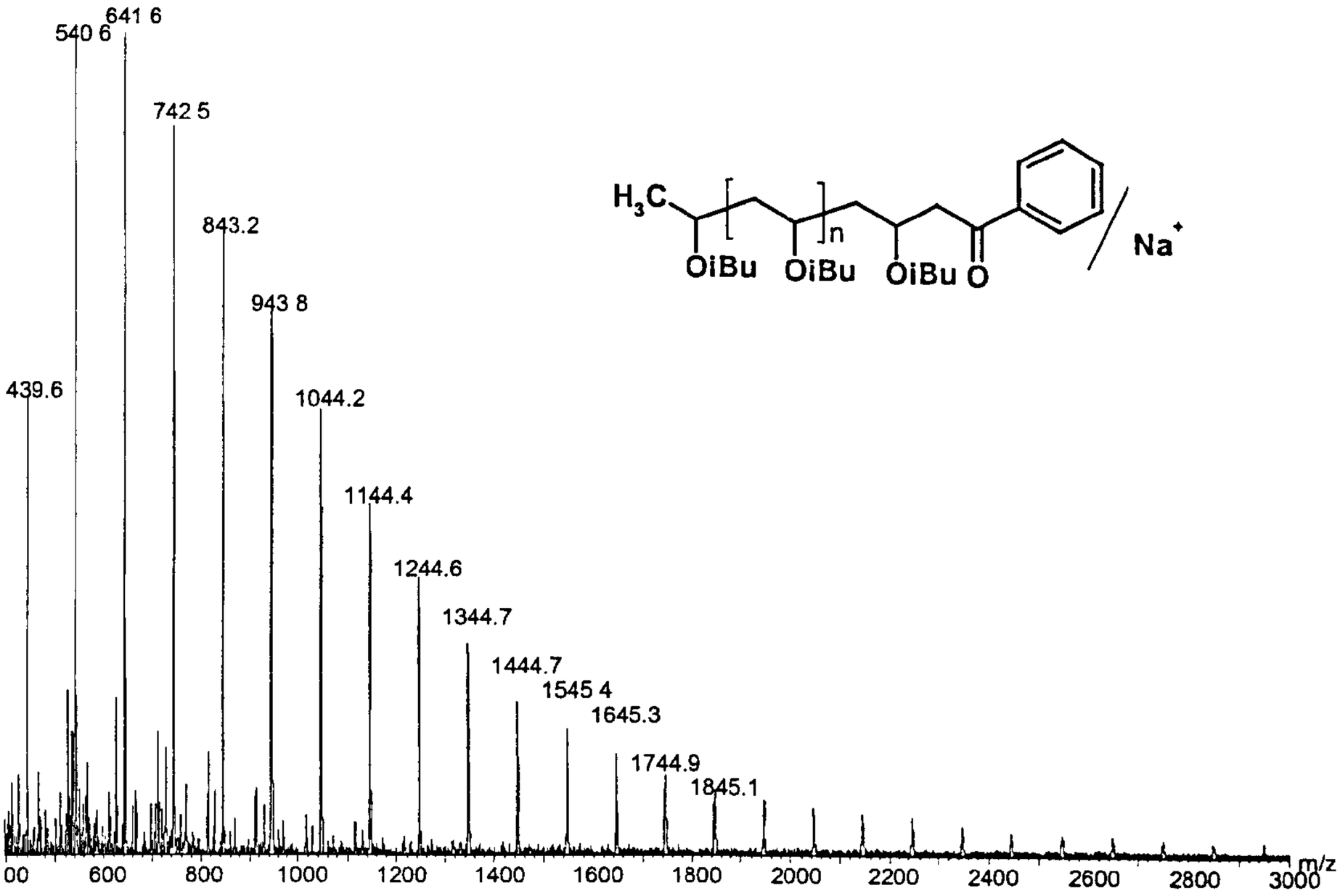


Figure 3-16: MALDI-TOF mass spectrum of OiBVE end-capped with SEE 1

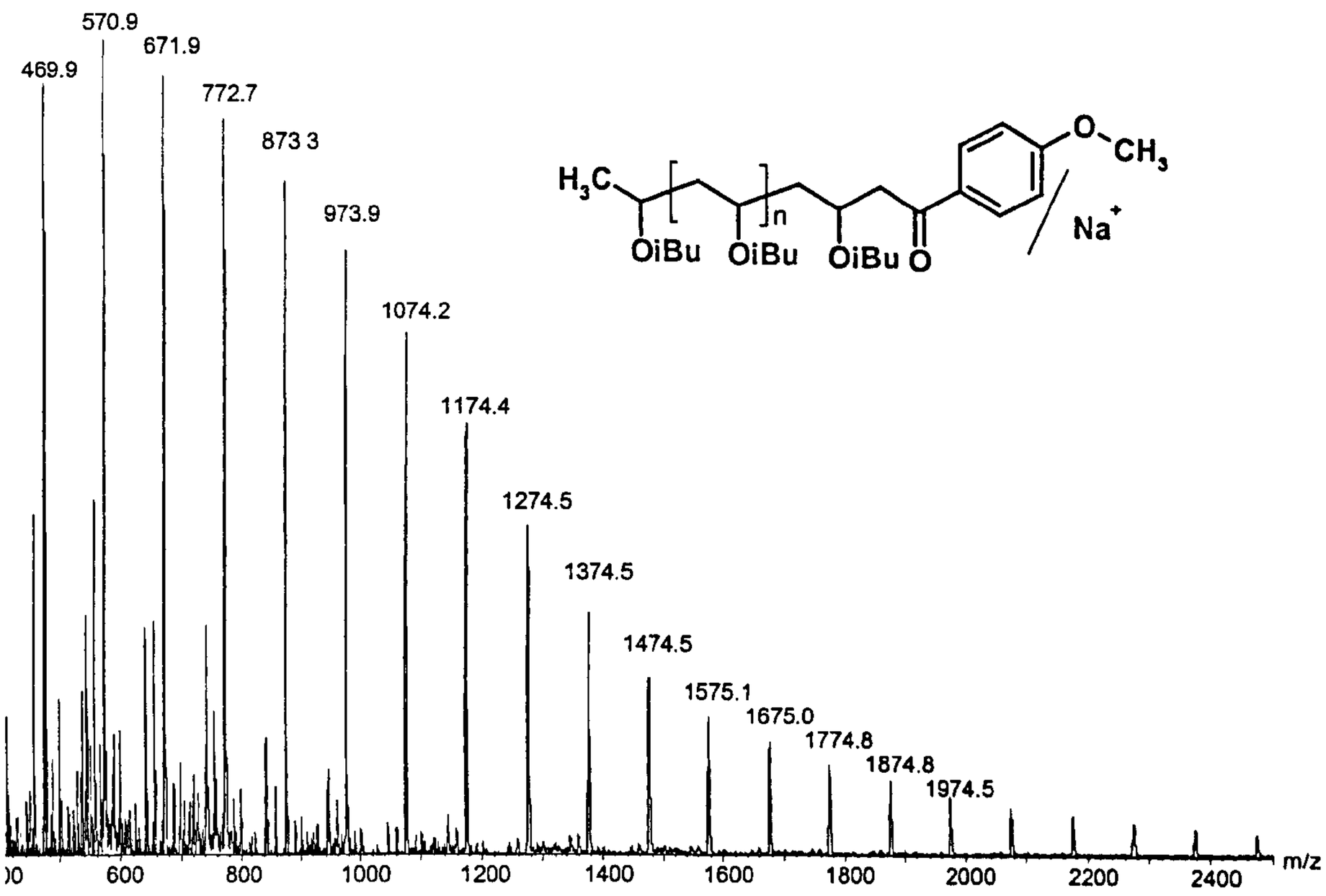


Figure 3-17: MALDI-TOF mass spectrum of OiBVE end-capped by SEE 2

Polymerisations conducted in the presence of **SEE 3** showed slightly different behavior at different polymerisation temperatures. Figure 3-18 and 3-19 show the MALDI-TOF mass spectra derived from polymerisations carried out at -16°C and 0°C. When the polymerisation temperature was –16°C the MALDI-TOF mass spectrum consists of two series of polymer ions. **SEE 3** partially capped the oligomer chain end and formed the oligomer series labeled with blue triangles. The other series labeled with the red triangles indicates the methoxy chain end due to the quenching reaction with methanol. However, at 0°C the alkylation reaction became dominant so that the MALDI-TOF mass spectrum of this sample shown in Figure 3-19 has one prominent series of polymer ions with residual masses that were assigned to the expected 3,3-dimethyl butanyl-2-one end group plus cationisation with sodium.

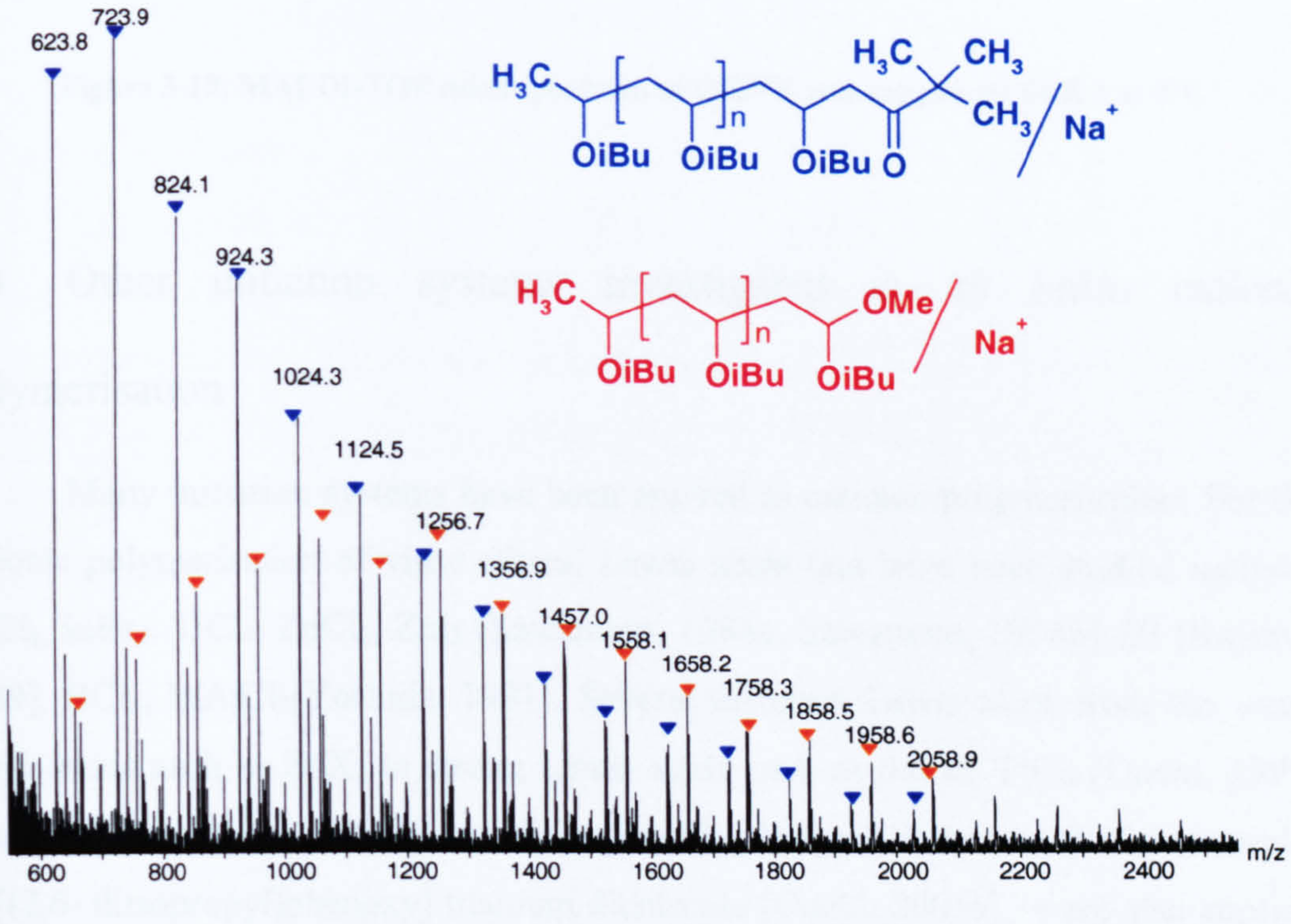


Figure 3-18: MALDI-TOF mass spectrum of OiBVE end-capped by SEE 3 at -16°C

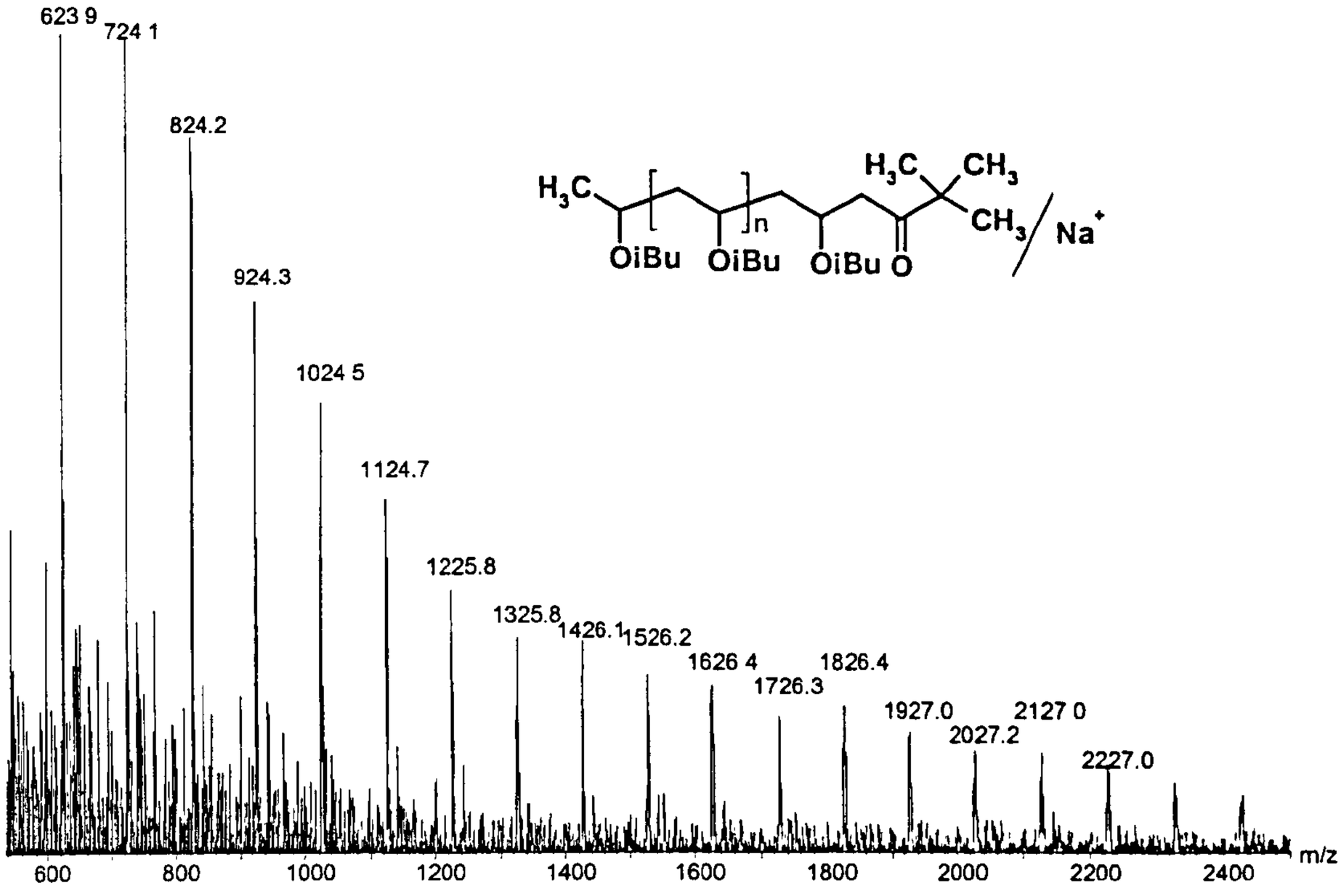


Figure 3-19: MALDI-TOF mass spectrum of OiBVE end-capped by SEE 3 at 0°C

3.4 Other initiation systems investigated in *ab initio* cationic polymerisation

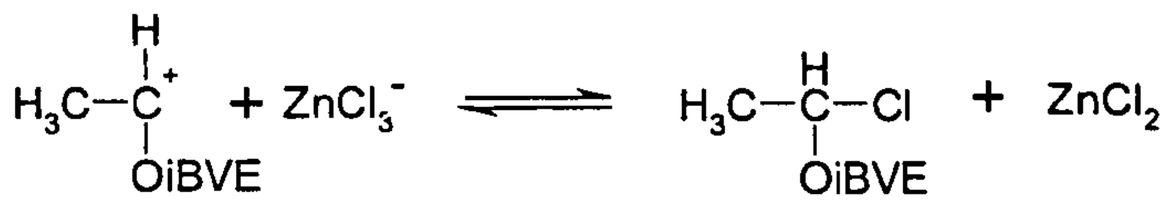
Many initiation systems have been applied in cationic polymerisation. For the cationic polymerisation of vinyl ethers, Lewis acids that have been studied include: $SnCl_4$, $SnBr_4$, $TiCl_4$, $ZnCl_2$, ZnI_2 [Sawamoto, 1988a; Sawamoto, 1988b], HI [Kojima, 1989], BCl_3, $EtAlCl_2$[Yoshida, 1991]. Several different Lewis acids from the weak Lewis acids such as ZnX_2 to strong Lewis acids such as $SnCl_4$, $TiCl_4$ [Ouchi, 1999; Ouchi, 2001b, Quchi, 2001c] and the especially designed Lewis acid, for example, bis[(2,6- diisopropyl)phenoxy] titanium dichloride [Ouchi, 2001a], were also applied in investigations of regioselectivity in the cationic polymerisation of cyclopentadiene and alkyl vinyl ethers.

For the purpose of searching for a suitable initiation system for *ab initio* cationic polymerisations different Lewis acids were explored.

3.4.1 $HCl/ZnCl_2$ initiation system

Polymerisation process analysis

Alkyl halide decomposition products can be reactivated with Lewis acid, leading to reversible termination as shown in scheme 3-2. Polymerisations involving reversible terminations are slow, but steady and controllable.



Scheme 3-2: Reversible termination with $ZnCl_2$

In this work $ZnCl_2$ was shown to be a more suitable Lewis acid for the cationic polymerisation of iBVE than $Yb(OTf)_3$, that it is produced a more well-defined polymerisation.

Figure 3-20 are the SEC overlays when $ZnCl_2$ was the Lewis acid. The polymerisation sample solutions were taken at different polymerisation times and were terminated by ammonium methanol solution. The properties of oligomers formed at these different polymerisation times were then analysed by SEC. The SEC results show that the peak elution time drifted to lower values as the polymerisation progressed. The shapes of the curves from 30 minutes to 165 minutes polymerisation time also changed. These data indicate an increase in molecular weight and a decrease in the molecular weight distribution of the oligomer samples before 165 minutes polymerisation time. However, the curves at 450 minutes and 600 minutes shifted to higher elution time indicating a reduction of molecular weight after 165 minutes of polymerisation time. Figure 3-21 more clearly indicates this change during the polymerisation. The calculated number average molecular weight of the oligomers at different polymerisation times increase from 3130 g mol^{-1} at 3 minutes to 4860 g mol^{-1} at 165 minutes, then reduce to 4350 g mol^{-1} at 600 minutes. PD shows the reverse trend. It reduces from 1.31 at 3 minutes to 1.21 at 165 minutes, then increase to 1.28 at 600 minutes. The polymerisation appears to be more controlled up to a certain point, when chains get longer with polymerisation time some termination occurs and

eventually this becomes significant and when chain transfer occurs they release H^+ that reinitiates and reduces the average molecular weight.

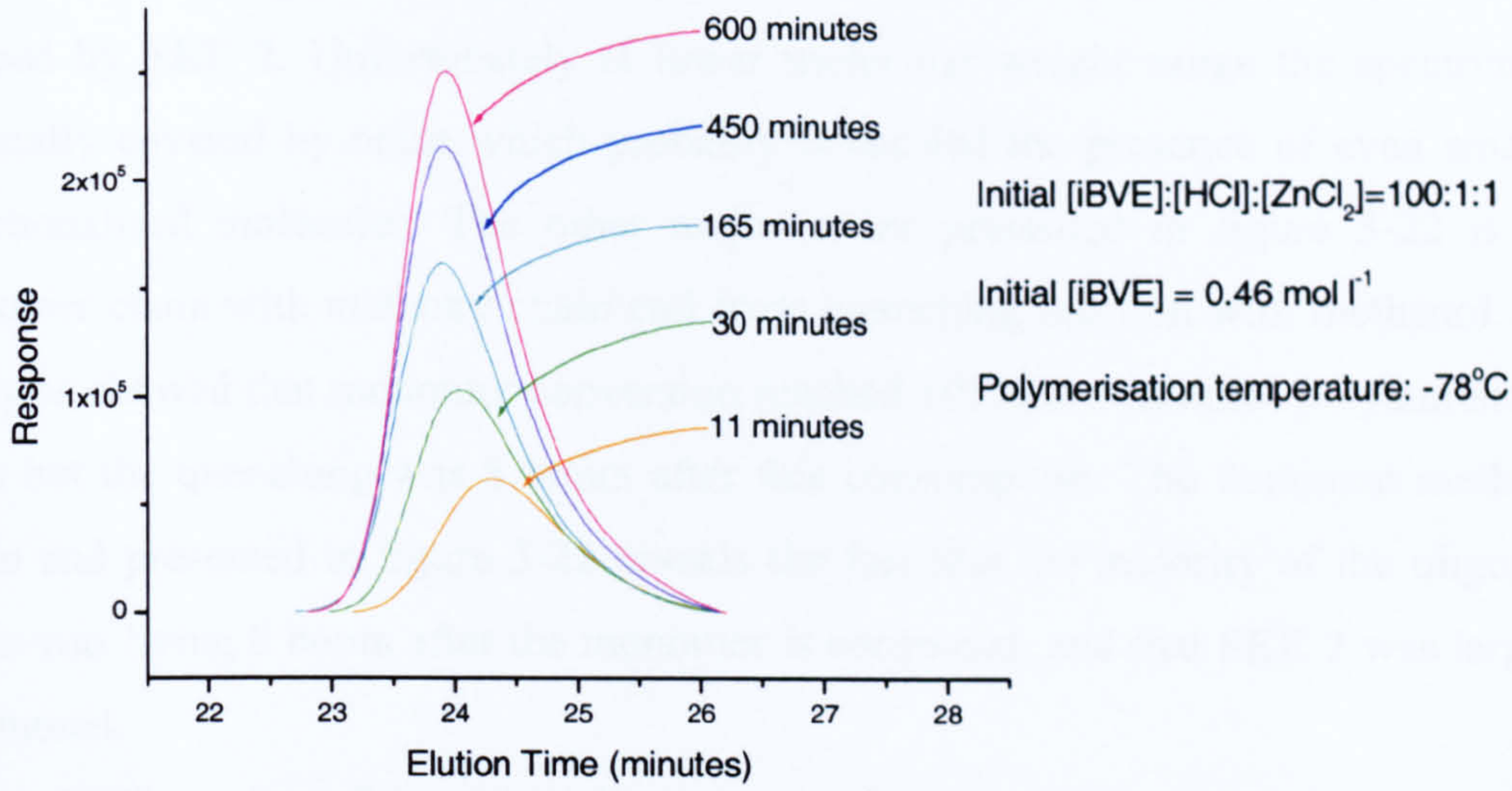


Figure 3-20: SEC analysis on polymerisation process with $ZnCl_2$ as Lewis acid

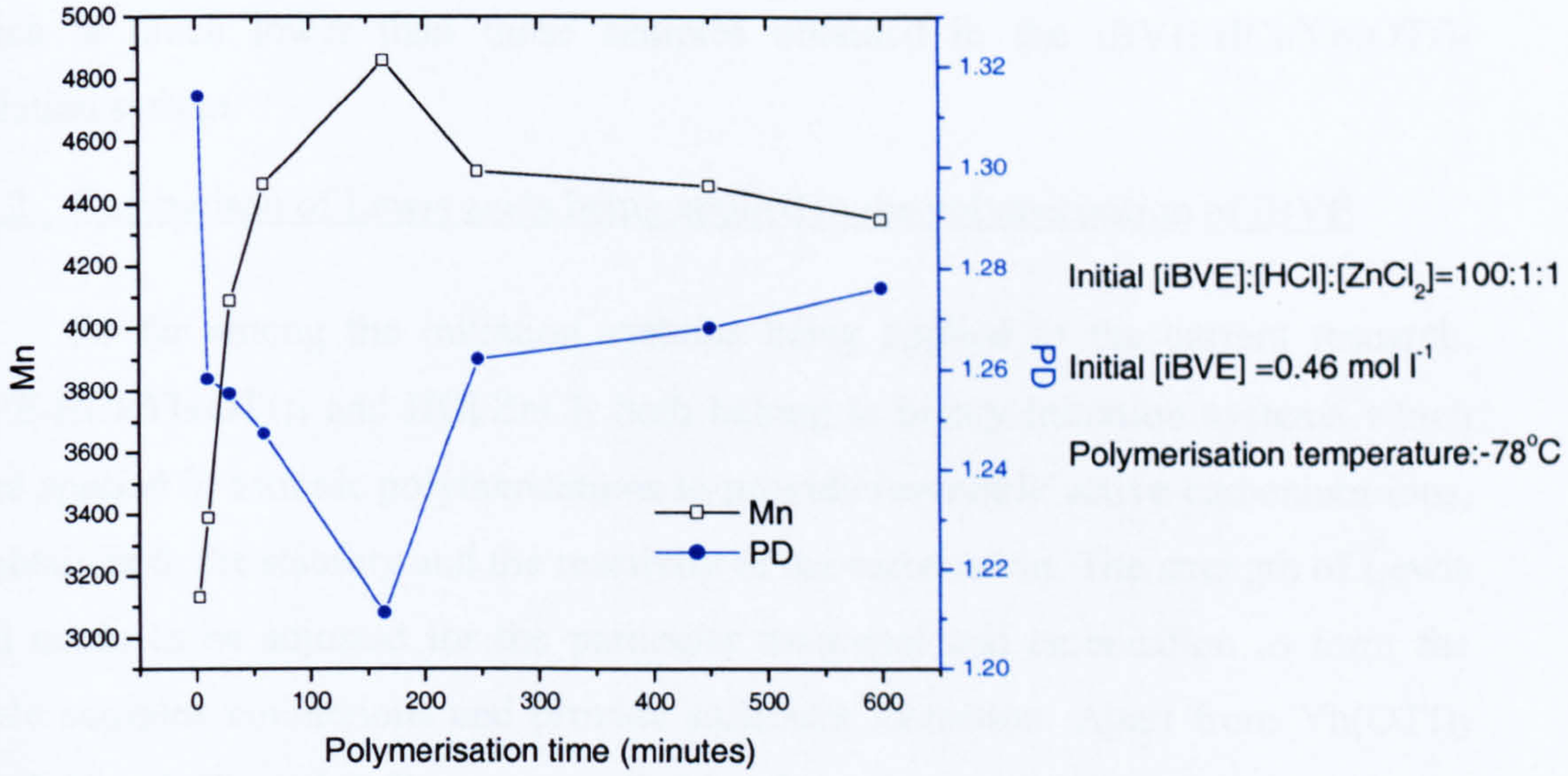


Figure 3-21: M_n and PD development during polymerisation with the $ZnCl_2$ as Lewis acid

Ab initio chain end functionalisation

The $HCl/ZnCl_2$ initiation system also supports end-capping of silyl enol ethers. Figure 3-22 is the MALDI-TOF mass spectra of OiBVE polymerised in the presence of **SEE 2**. Probably due to the higher relative reactivity of end-capping of **SEE 2** over chain propagation, only very short silyl enol ether functionalised

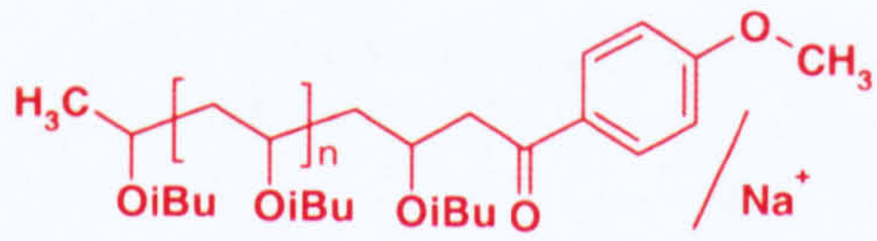
oligomers were presented in this spectrum as indicated with red triangle in figure 3-22. The signal with the ion mass of 100n+74 indicates the OiBVE end-capped by **SEE 2.** For example the oligomer with ion mass of 474.0 indicates a trimer end-capped by **SEE 2**. Unfortunately at lower molecular weight range the spectrum is generally covered by noise which probably concealed the presence of even smaller functionalised molecules. The other major series presented in figure 3-22 is the oligomer chain with methoxy chain end from quenching reaction with methanol. GC analysis showed that monomer conversion reached 100% at 5 minutes polymerisation time but the quenching was 8 hours after this consumption. The dominant methoxy chain end presented in figure 3-22 reveals the fact that the majority of the oligomer chain was living 8 hours after the monomer is consumed, and that **SEE 2** was largely consumed.

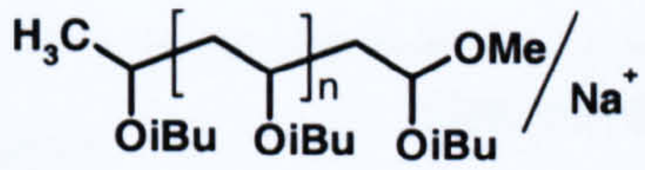
SEC overlay of the same oligomer sample gave a trimodel molecular weight distribution which also supports the formation of small molecules. ^1H NMR analysis gives 34% of the chain end functionality of the oligomer sample shown in figure 3-22, which is much lower than those samples obtained in the iBVE-HCl/$Yb(OTf)_3$ initiation system.

3.4.2 Comparison of Lewis acids being applied in the polymerisation of iBVE

So far among the initiation systems being applied in the current research, iBVE-HCl/$Yb(OTf)_3$ and HCl/$ZnCl_2$ both belong to binary initiation systems which were applied in cationic polymerisations to provide reversibly active carbenium ions, to obtain both the stability and the reactivity of the carbocation. The strength of Lewis acid needs to be adjusted for the particular monomer and carbocation to form the stable complex counterions and provide sufficient ionisation. Apart from $Yb(OTf)_3$ and $ZnCl_2$, $SnCl_4$ and $SnBr_4$ were applied by the author as Lewis acid as well in the polymerisation and *ab initio* chain end functionalisation of isobutyl vinyl ether. The known relative strength among them is:

$$ZnCl_2 < SnBr_4 < SnCl_4$$





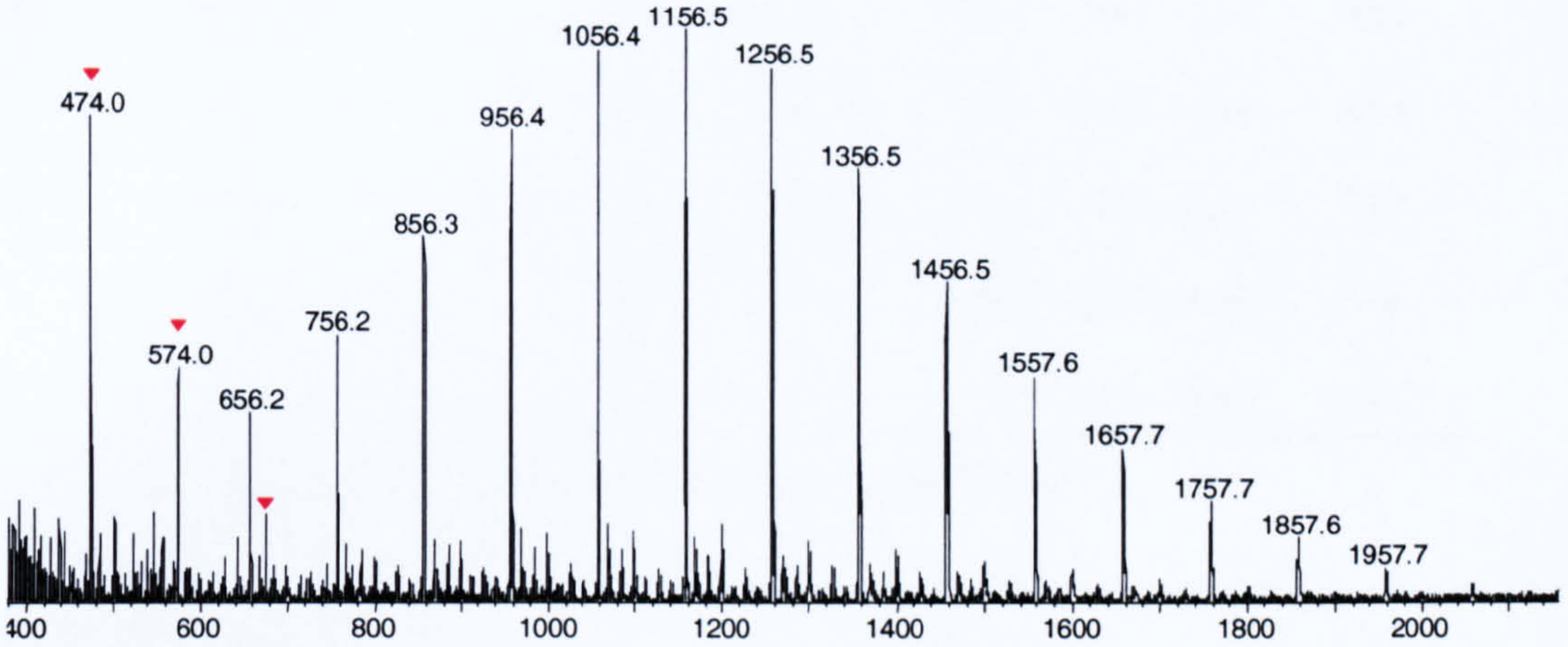


Figure 3-22: $ZnCl_2$ mediated *ab initio* chain end functionalisation

[iBVE]:[HCl]:[SEE2]:[$ZnCl_2$]=10:1:1:1, Initial [M]=0.46 mol l^{-1}, polymerisation temperature: -78°C, M_n=460, PD=2.19, Fn=34.0%

Table 3-4 compares protonic acid (HCl) initiation to two-component initiations with 4 different Lewis acid in the cationic polymerisation of isobutyl vinyl ether.

At a polymerisation temperature of –15°C, compared with the binary initiation systems HCl gave a very broad molecular weight distribution. Yb(OTf)$_3$, a strong Lewis acid, produces oligomer with broad molecular weight distribution as usual. Polymerisations using $SnCl_4$ and $SnBr_4$ as Lewis acids showed similar M_n and PD value to each other. $SnBr_4$ produces OiBVE with slightly narrower molecular weight distribution. In this research $ZnCl_2$ was only applied at -78°C. It could be this low polymerisation temperature as well as the relatively weak Lewis acidity that led to the lowest PD value in the table. Although water initiation was largely suppressed at this low temperature, the lower M_n than theoretical value still indicates the presence of side reactions.

Table 3-4: A comparison of different Lewis acids on polymerisation of iBVE

Monomer	Lewis acid	Time min	SEE	[M] mol l^{-1}	Temperature °C	[M]:[I]	M_n	PD	Conversion %
iBVE	$Yb(OTf)_3$	10	None	0.50	-15	10:1	990	2.75	89.5
	$SnCl_4$	90		0.50	-15	10:1	1010	1.89	68.4
	$SnBr_4$	90		0.50	-15	10:1	1000	1.76	82.4
	$ZnCl_2$	600		0.46	-78	100:1	4260	1.29	100
	HCl	120		0.53	-15	10:1	2340	4.98	98.7

Polymerisation conditions are the same unless otherwise listed in the table

3.5 Chapter summary

Cationic polymerisation of isobutyl vinyl ether was performed with the potential water tolerant Lewis acid, ytterbium triflate, as co-initiator. The polymerisation analysis showed that the polymerisation system is not a living system and the polymerisation temperature could seriously effect the polymerisation through its influence on the side reactions.

Trimethyl-(1-phenyl-vinyloxy)-silane, trimethyl-(1-4-methoxyphenyl-vinyloxy)-silane and 2,2-dimethyl-1-methylene-propoxy)-trimethyl-silane were applied as end-capping agents and were alkylated *in-situ* by the propagating carbocationic chain end and successfully attached to the oligomer chain.

Generally, the polymerisation of iBVE gave functionalised OiBVEs of lower molecular weights and broader molecular weight distributions when performed in the presence of **SEE 1** or **SEE 2** than when the reaction was carried out in their absence. High chain end functionality was obtained at various polymerisation temperatures. A*b initio* cationic polymerisation in the presence of **SEE 3** gave functionalised OiBVEs with lower molecular weights and narrower molecular weight distributions than polymerisations carried out in the absence of the silyl enol ether.

The methodology relies on the fact that alkylation of silyl enol ethers by the propagating macrocarbocation can occur at a rate that lies between the rate of propagation and the normal rates of termination or side reactions in the non-living

polymerisation. Thus propagation occurs but the normal termination reaction is suppressed so that the majority of the termination reactions are due to reaction of the silyl enol ether with a propagating chain end. Further optimisation of the methodology and extension to other systems is to be discussed in the following chapter.

Chapter 4. $SnCl_4$ Catalysed *ab Initio* Cationic Polymerisation

4.1 Introduction

4.1.1 Application of $SnCl_4$ as co-initiator

As introduced in chapter 1 the direction of molecular engineering is toward controlled polymerisation so that the well-defined polymer can be produced. The most fundamental feature of the well-defined polymer is the control of molecular weight and molecular weight distribution. Other structural factors that should or maybe controlled include end groups, pendant groups, sequence (the arrangement of constitutional repeat units and segments along a main chain), steric structure and three-dimensional or spatial shape [Sawamoto, 1992; Sawamoto, 1993; Sawamoto, 1996].

Cationic polymerisation of vinyl ether monomers has been thoroughly investigated by Sawamoto and Higashimura since 1979 [Higashimura, 1979], and well-controlled systems have been established. Various Lewis acids have been examined in the binary initiation systems, including ytterbium triflate ($Yb(OTf)_3$) as a potential water-resistant Lewis acid as introduced in chapter 3. $Yb(OTf)_3$ was applied in *ab initio* chain end functionalisation (described in chapter 3) and highly functionalised homotelechelic oligo (isobutyl vinyl ether)s were produced. However the obtained functionalised oligomers have broad molecular weight distributions.

Since 1989, well-defined cationic polymerisations have been carried out using tin tetrachloride ($SnCl_4$) as the Lewis acid [Kojima, 1989] and living cationic systems were produced [Ishihama, 1990]. We have applied $SnCl_4$ as the Lewis acid in our *ab initio* end-capping research for several purposes. Firstly, we wanted to see if $SnCl_4$ mediated cationic polymerisation supported the *ab initio* chain end functionalisation. Secondly, a controlled cationic system was required to compare the relative end-capping rate and chain propagation rate. In a controlled *ab initio* chain end functionalisation the only possible termination reaction is end-capping (other side reactions should be suppressed so that only chain propagation and end-capping can occur during the polymerisation and these aspects can be investigated). The third purpose was to investigate the effects of the presence of silyl enol ethers on the known cationic system. Finally we wanted to set up a novel cationic polymerisation

system in which the oligomer's molecular weight, polydispersity and chain end functionality could all be regulated.

Polymerisation temperature generally has a significant influence on cationic polymerisation. In our former research it has also been observed that polymerisation temperature affects chain end functionality.

4.1.2 End-capping with silyl enol ethers in cationic polymerisation

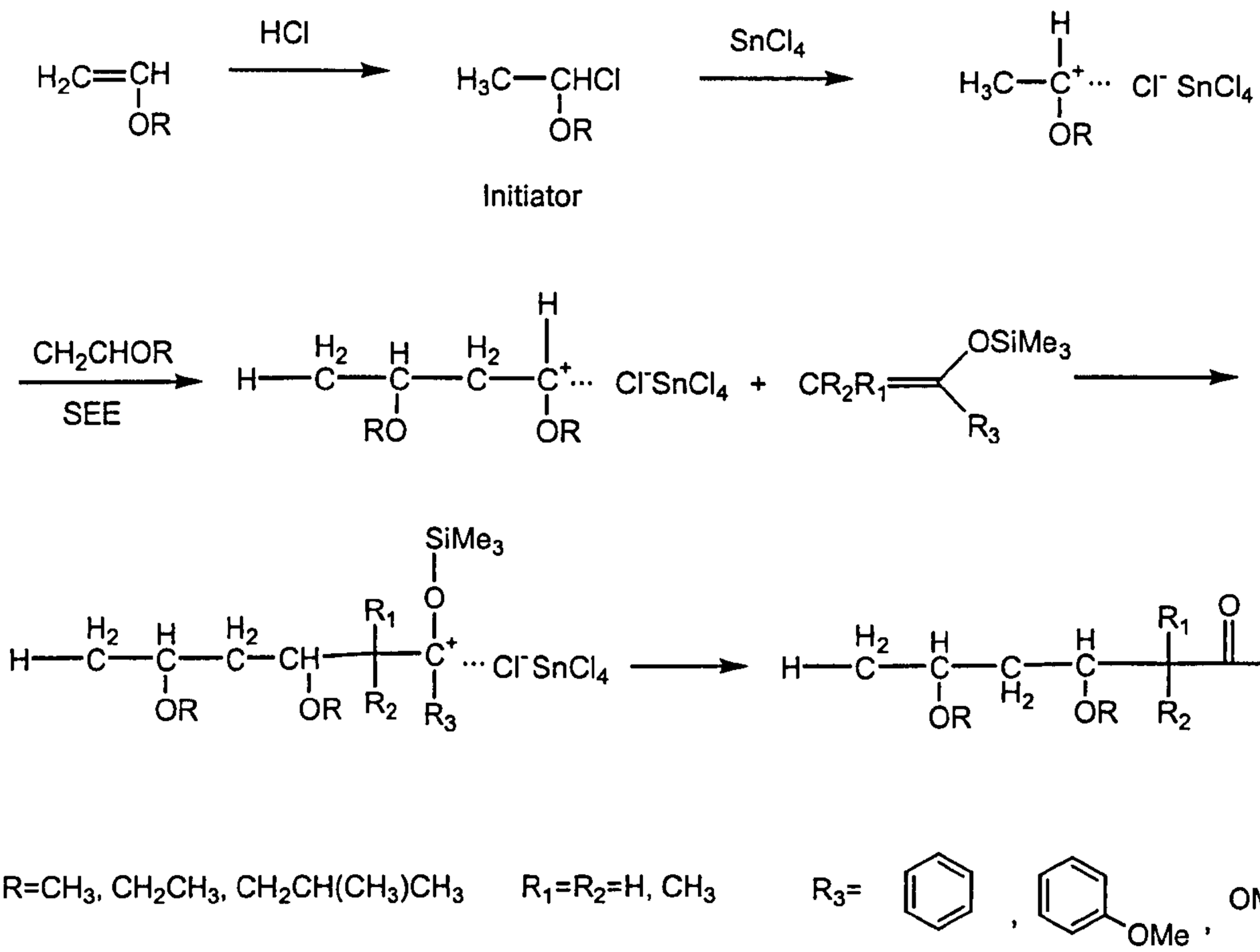
As introduced in chapter 1 the formation of multi-armed block copolymers via the coupling reaction between the multifunctional silyl enol ethers and living carbocationic chain ends has also been explored by Sawamoto's group from 1993 to 1996 [Fukui, 1993; Fukui, 1994a; Fukui, 1994b; Miyashita, 1994; Sawamoto, 1994; Fukui, 1995a; Fukui, 1995b; Fukui, 1996a; Fukui, 1996b]. The use of end-capping in cationic polymerisation dates back to 1982 [Sawamoto, 1982a] when sodium β-naphthoxide was applied as an end-capping agent in the cationic polymerisation of styrene for the purpose of kinetic research on the polymerisation process. Until now end-capping research in cationic polymerisations has generally required living systems, so that the end-capping reagents cap the living chain ends and produce terminal functionalities. Under these conditions, a large selection of end-capping agents can be applied in end-capping. However this also requires living systems, which limits its industrial application.

Also as described in chapter 1, in *ab initio* chain end functionalisation the silyl enol ethers compete with the monomer from the beginning of polymerisation to cap the oligomer chain end. We intended to set up a system in which the end-capping of silyl enol ether occurs at a similar rate to that of chain propagation. Thus functionalised oligomer chains, with a certain degree of polymerisation, could be formed even though the cationic system is not living. Ideally, the rate of selected end-capping allows the consumption of monomer to form oligomer chains but the chains are capped before other side reactions occur to reduce other chain ends and unite the oligomer chain length. However, under such conditions, small amounts of fast side reactions could still occur.

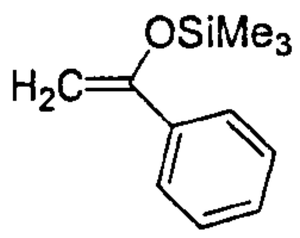
It is difficult to measure the chain propagation and end-capping rates in the current cationic polymerisations because of the very high chain propagation rates in the selected systems and also uncertainty in defining the ion pairing state of the

propagating chain end. Experiments were designed to infer more information about this *ab initio* chain end functionalisation.

The *ab initio* end-cappings (Scheme 4-1) were performed at temperatures ranging from –78 °C to room temperature (21°C). Iso-butyl vinyl ether (iBVE), ethyl vinyl ether (EVE) and methyl vinyl ether (MVE) were applied as monomers. 6 synthesised and commercial silyl enol ethers (**SEEs**, shown in Figure 4-1) were applied in end-capping. All 6 silyl enol ethers were applied in the polymerisation of iBVE. **SEE 1** was applied in the polymerisation of EVE at various polymerisation temperatures. **SEE 1** and **SEE 4** were applied in the polymerisation of MVE. The iBVE-HCl was applied as an initiator and $SnCl_4$ as a co-initiator. At -78°C and in the presence of *n*-Bu_4NCl, OiBVEs with lower molecular weight distributions were produced while the end-capping rates were maintained. Side reactions which present in the current polymerisations were examined by MALDI-TOF mass spectrometry and NMR.

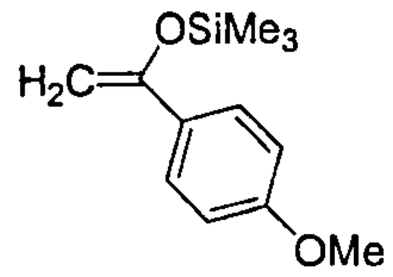


Scheme 4-1: *ab initio* chain end functionalisation in cationic polymerisation of vinyl ethers



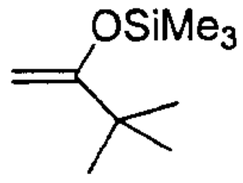
silyl enol ether 1

Trimethyl-(1-phenyl-vinyloxy)-silane



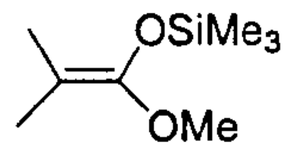
silyl enol ether 2

[1-(4-Methoxy-phenyl)-vinyloxy]-trimethyl-silane



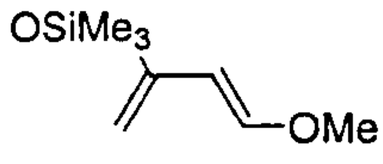
silyl enol ether 3

(1-*tert*-Butyl-vinyloxy)-trimethyl-silane



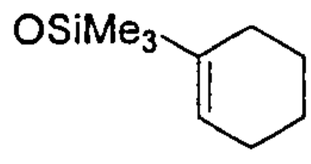
silyl enol ether 4

(1-Methoxy-2-methyl-propenyloxy)-trimethyl-silane



silyl enol ether 5

(3-Methoxy-1-methylene-allyloxy)-trimethyl-silane



silyl enol ether 6

(Cyclohex-1-enyloxy)-trimethyl-silane

Figure 4-1: Silyl enol ethers being applied in *ab initio* chain end functionalisation

4.2 Results and discussion

4.2.1 Polymerisation of iBVE at different temperatures -- SEC results

Table 4-1 shows the polymerisation data for OiBVE samples obtained at different polymerisation temperatures, without end-capping. It can be seen from the table that the use of low temperature and the added nucleophile led to the formation of well-defined oligomers. The highest polymerisation temperature does not produce the lowest molecular weight, as may be expected, but it does produce the broadest molecular weight distribution. The results obtained for the polymerisation carried out at 21°C were complicated and therefore difficult to explain. As discussed in the previous chapter, polymerisation temperature does not seriously affect the polymerisation because of the generally low absolute activation energy in cationic polymerisation. The activation energy data of the chain propagation reaction of isobutyl vinyl ether cannot be obtained. However, the data in table 4-1 implies that

higher temperature leads to an increase in the chain propagation rate, also the rates of the side reactions increase, resulting in a broad molecular weight distribution. The data in table 4-1 indicates that the rate of chain propagation is substantially higher than the side reactions rates. At low temperature the increased degree of polymerisation is probably due to the reduction of side reactions. The balance of the chain propagation and side reactions at different temperatures determines the properties of the resulting oligomers.

Table 4-1: Results of the polymerisation of OiBVE samples without end-capping

Monomer	Additive[α]	Temp. °C	M:I:L:SEE[β]	Conversion %	Polyn.Time Minutes	M_n	M_w	PD
iBVE	None	21	10:1:0.5:0	58.1	60	870	1950	2.24
	None	0		59.4	60	770	1350	1.74
	None	-15		57.8	60	800	1400	1.76
	n-Bu_4NCl	-15		81.8	60	760	1220	1.62
	None	-78		100	60	940	1460	1.56
	n-Bu_4NCl	-78		100	5	1370	1510	1.10

[α]: The ratio of $SnCl_4$: *n*-Bu_4NCl = 0.5: 0.75 when this additive is applied

[β]: M:I:L:SEE means the initial concentration ratio of monomer, initiator, Lewis acid and silyl enol ether, and the initial monomer concentration [iBVE]=0.38 mol L^{-1}

4.2.2 MALDI-TOF analysis of the oligomers

Quantitative comparison of different chain ends required the use of MALDI-TOF MS in order to analyse the significance of different side reactions under various polymerisation conditions. The quantitative reliability of MALDI-TOF mass spectra needs to be discussed for this requirement. This matter is discussed in detail in chapter 5 but a brief introduction is given here.

Reports showed that MALDI-TOF MS is not regarded as a reliable technique for average molecular weight and molecular weight distribution calculation because of the possible selective polymer chain desorption and selective ionisation [Hanton,

1999; Nielen, 1999]. Reproducible sample preparation, comprehensive sample expression and non-discriminable ionisation need to be satisfied in order to obtain a meaningful comparison of the relative intensities of signals within a certain mass range. These conditions can be satisfied and the MALDI-TOF mass spectra can be used to illustrate the detailed polymerisation process.

A MALDI-TOF mass spectrum of the product derived from the polymerisation at -78°C in the presence of *n*-Bu_4NCl is shown in Figure 4-2.

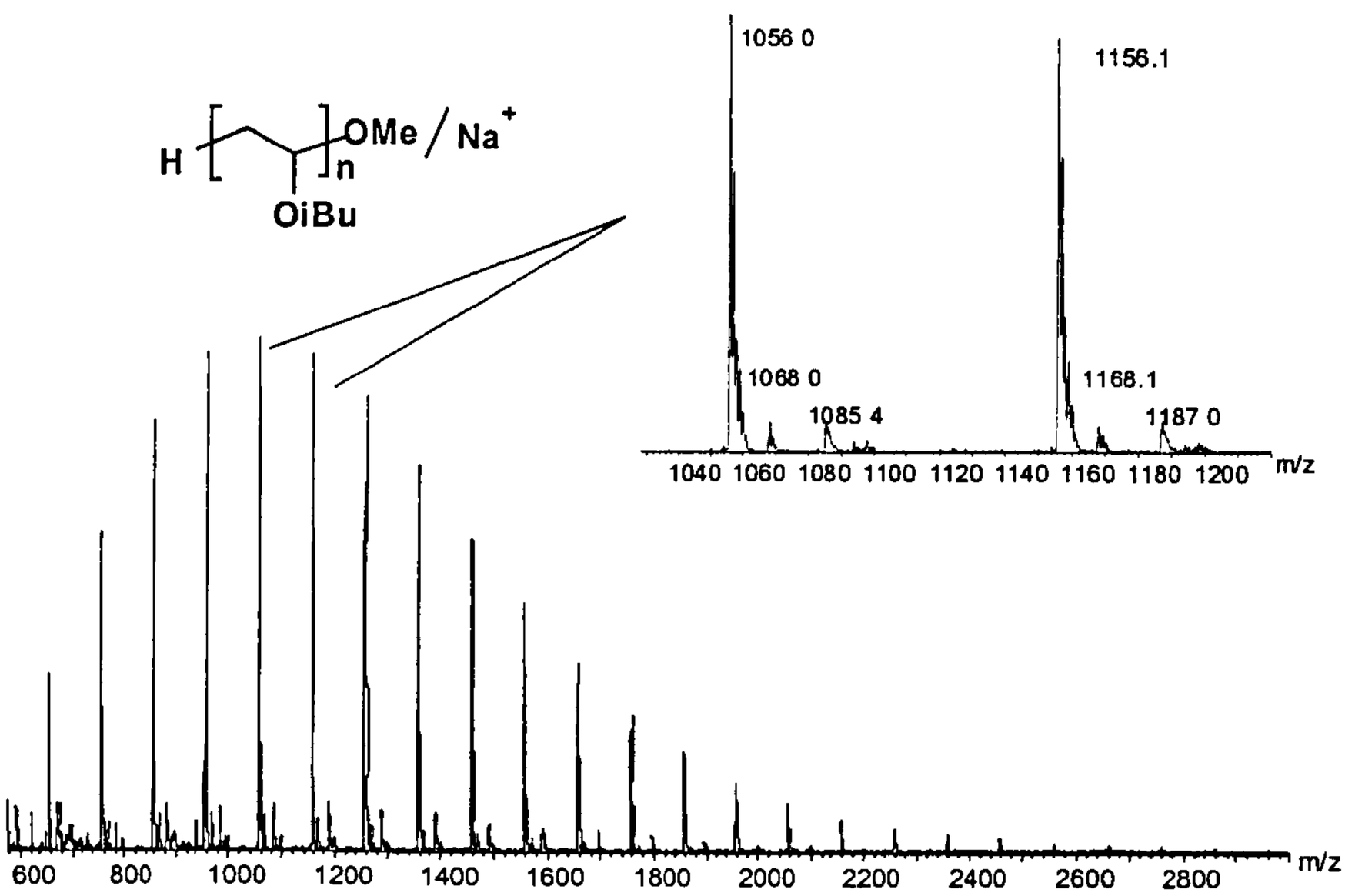


Figure 4-2: MALDI-TOF spectrum of one of OiBVE sample

[iBVE]:[iBVE-HCl]:[SnCl4]:[*n*-Bu4NCl]=10:1:1:0.5:0.75, initial [iBVE]=0.38 mol L^{-1} Polymerisation time: 5minutes, polymerisation temperature: -78°C, M_n =1370, PD=1.10

It is composed predominantly of a series of mass peaks that are separated by the repeat mass of the iBVE repeat unit (100 g mol^{-1}). Each peak can be accounted for by the structure shown in the insert, i.e., the oligomers possess α-H's, ω-methoxy end groups and the cationisation is due to addition of a single sodium ion except where otherwise indicated. The addition of methanol resulted in capping of any remaining living chains with methoxy chain ends. This data clearly indicates that, at -78°C this polymerisation is almost a living or pseudo-living system, i.e., most of the chain ends are active at the end of the monomer propagation and are thus able to react with MeOH. However, small peaks at $m/z = 100n + 68$ are observed. The other peak series

at m/z = 100n + 85 is not easily assigned. The best possible assignment is the aldehyde chain end with potassium ionisation. Also small amounts of the diisobutanol chain end were detected in this spectrum.

However, in the absence of the nucleophile and at higher polymerisation temperature, side reactions were more predominant. Figure 4-3 shows the MALDI-TOF mass spectra of 4 oligo(isobutyl vinyl ether)s synthesised at various temperatures in the absence of an added nucleophile. SEC data of these samples are listed in table 4-1. Figure 4-4 shows an expansion of MALDI-TOF mass spectra of figure 4-3 that contains one repeat unit of the figure in which detailed different oligomer chains can be observed.

All oligomer samples have more than one series of signals in their MALDI-TOF mass spectrum due to the different chain ends present in the sample. The detailed side reactions that could lead to these different chain ends will be discussed later.

The prominent chain end group present is very different depending on the polymerisation temperature. It can be seen that at 21°C there is no living chain end left at quenching because no methoxy chain end is observed in the spectrum. A considerable amount of alkene chain end (with the ion mass of 100n+24) and a small amount of diisobutanol chain end (with the ion mass of 100n+98) were apparent at this temperature. At 0°C the diisobutanol chain end becomes dominant and a small amount of alkene and methoxy chain ends were also found, indicating that the small amount of living chain end was terminated at quenching. At -15°C the methoxy chain end becomes more dominant and diisobutanol is also present in a significant quantity. A small amount of proton ionised secondary alcohol chain end appeared. At -78° the increased methoxy chain end and decreased diisobutanol and alkene chain ends indicate that more unreacted chain ends were present at quenching, and that low temperature disfavors the side reactions that lead to diisobutanol and alkene chain ends. So the conclusion is that at -78°C a fraction of the chains are still active at the end of the polymerisation but side reactions still occur, whereas at 21°C all of the chains are terminated prior to addition of ammonia/methanol solution.

Figure 4-3: MALDI-TOF mass spectra of oligo(isobutyl vinyl ether)s synthesised at different temperatures without end-capping

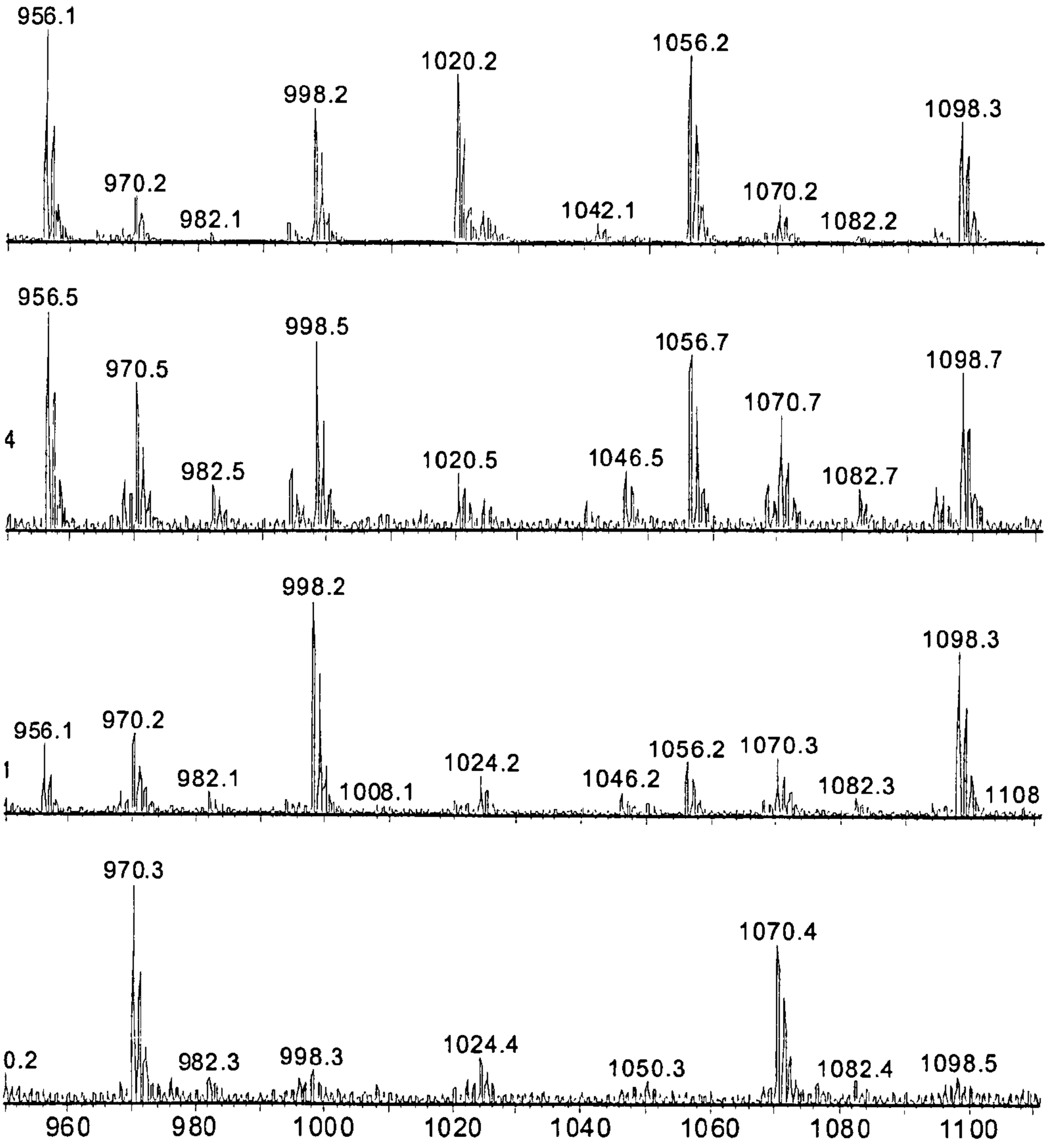


Figure 4-4: Expanded MALDI-TOF mass spectra of oligo(isobutyl vinyl ether)s synthesised at different temperatures,

From the top spectrum to the bottom spectrum, polymerisation tempeartures are -78°C, -15°C, 0°C and 21°C, [iBVE]:[iBVE-HCl]:[SnCl4]=10:1:1:0.5, initial monomer concentration: [iBVE]=0.38 mol L^{-1}, Polymerisation time: 60 minutes

Figure 4-5 shows the enlarged MALDI-TOF mass spectrum of one of the oligomer samples containing the polymer ion series due to side reactions. The structures of different chain ends are postulated and labeled on each mass peak. There are 9 series of different chain ends resulting from these polymerisation conditions. **1** is the methoxy chain end from the quenching process. **2** is the aldehyde chain end which was also observed by Katayama [Katayama, 2001a]. There is no clear postulation for

3, but the primary alcohol chain end is the best matched structure for the corresponding signal. However, a reasonable mechanism for formation of this primary alcohol chain end cannot be suggested. **4** and **5** contain internal alkene methoxy and internal alkene aldehyde chain ends respectively. These chain ends have not been reported previously. **6** is the diisobutanol chain end; it frequently appears as a result of the main side reaction and is also reported by Katayama [Katayama, 2001a]. **7'**, with an ion mass of 100n+20 Daltons, is best matched by a protonated secondary alcohol chain end. Another much smaller signal with a mass of 100n+42 Daltons, recorded as **7**, is suggested to be the same secondary alcohol chain end as the sodium salt. **8** is the alkene chain end, resulting from a chain transfer reaction.

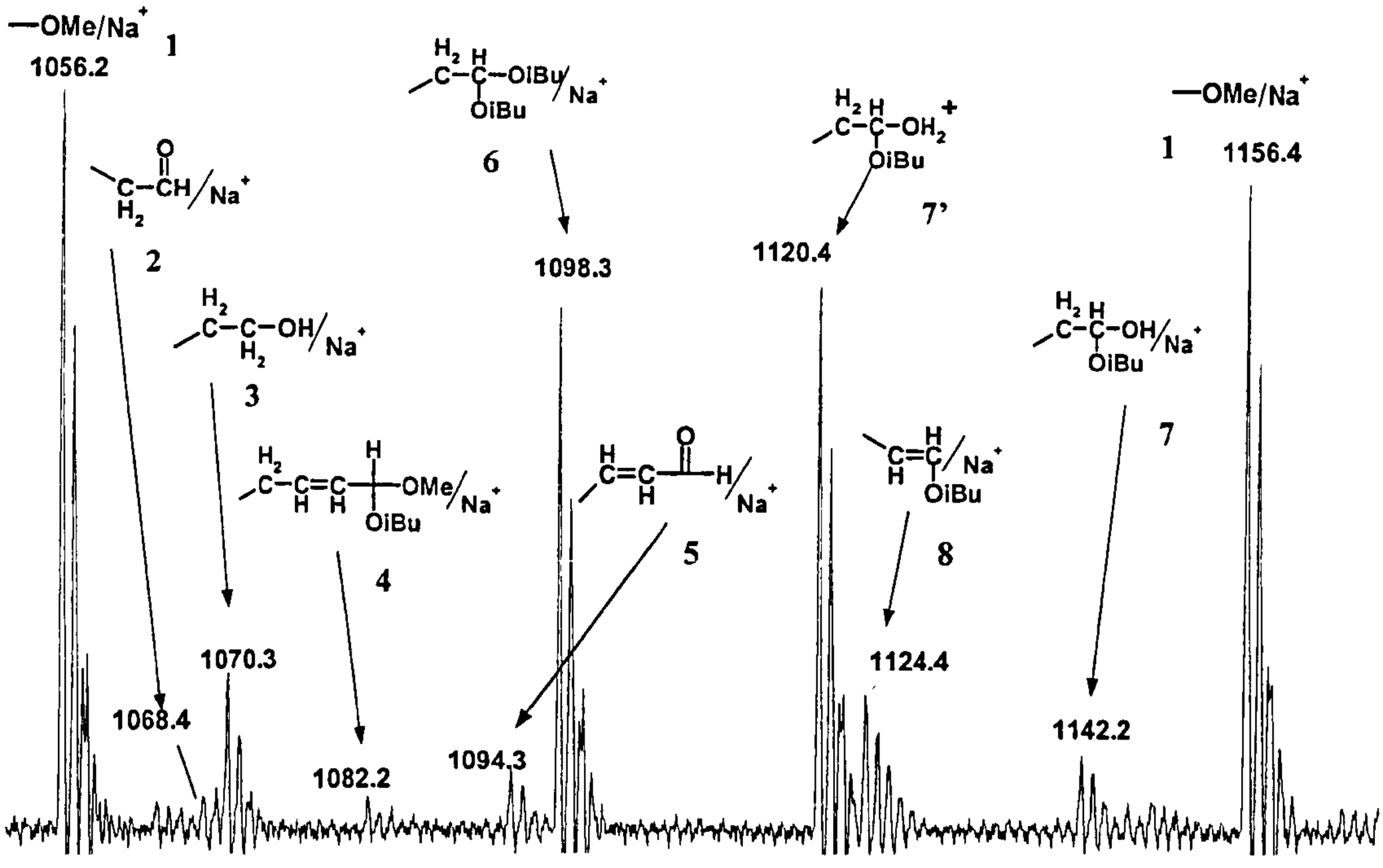


Figure 4-5: Detailed polymerisation side reaction analysis from MALDI-TOF mass spectrum

[iBVE]: [iBVE-HCl]: [$SnCl_4$]=10:1:0.5, initial monomer concentration: 0.38 mol L^{-1}, polymerisation temperature: -78°C, M_n =940, PD=1.56, polymerisation time=60minutes

Table 4-2 gives the assignments of the different chain ends observed in the polymerisation of isobutyl vinyl ether without end-capping, including the chain ends shown in figure 4-5. Monoisotope theoretical and experimental masses are compared in table 4.2. Again, the attachments of various ions to the same chain end were also listed in the table. For example, **2'** contains the protonated aldehyde chain end, **6'** has

the diisobutanol chain end with the attachment of a potassium ion. **9** could be the internal alkene secondary alcohol chain end; it is not possible to confirm this because its theoretical ion mass overlaps with **2**. The same situation was observed with **10**, and again the postulated structure could not be confirmed.

Table 4-2: Assignments of different OiBVE chain ends observed by MALDI-TOF MS

number	OiBVE with different ω-ends	OiBVE mass/charge* *m/z*	
		Theoretical	Experimental
1	H-(iBVE)$_{10}$-OCH_3/Na^+	1055.9	1056.2
2	H-(iBVE)$_{10}$-CH_2-CHO/Na^+	1067.9	1068.4
3	H-(iBVE)$_{10}$-CH_2-CH_2OH/Na^+	1069.9	1070.3
4	H-(iBVE)$_9$-CH_2-CH=CH-CH(OiBu)-OCH_3/Na^+	1081.9	1082.2
5	H-(iBVE)$_{10}$-CH_2-CH=CH-CHO/Na^+	1093.9	1094.3
6	H-(iBVE)$_{10}$-(OiBu) /Na^+	1098.0	1098.3
7	H-(iBVE)$_{11}$-OH/Na^+	1142.0	1142.2
8	H-(iBVE)$_9$-CH=CH(OiBu) /Na^+	1023.9	1024.4
7'	H-(iBVE)$_{11}$-OH/H^+	1120.0	1120.4
2'	H-(iBVE)$_{10}$-CH_2-CHO/H^+	1045.9	1046.2
6'	H-(iBVE)$_{10}$-(OiBu) /K^+	1114.1	1114.5
9	H-(iBVE)$_9$-CH_2-CH=CH-CH(OiBu)-OH/Na^+	1067.9	-
10	H-(iBVE)$_9$-CH_2-CH=CH-CH(OiBu)-OiBu/Na^+	1124.0	-

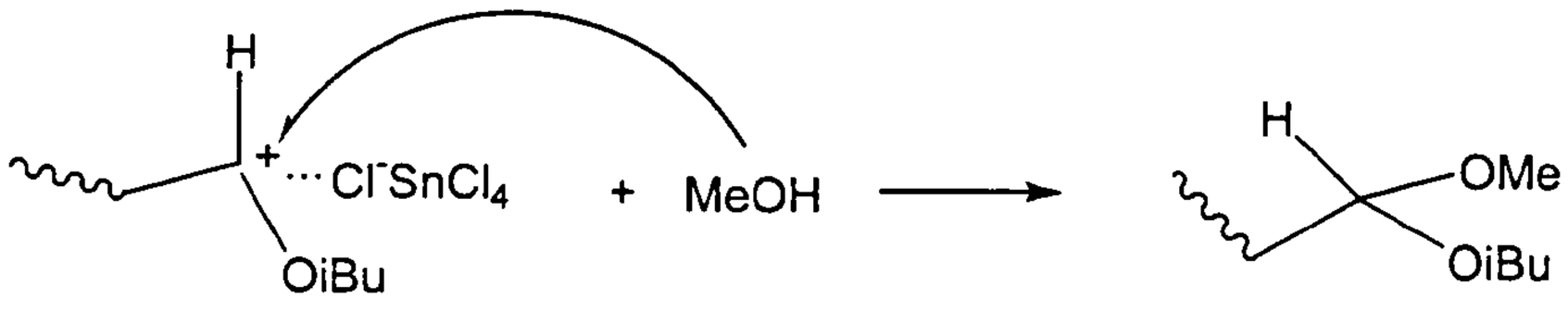
*: Monoisotope oligomer mass was calculated or obtained for both theoretical and experimental value.

4.2.3 Analysis of side reactions

Various oligomer chain ends appeared in MALDI-TOF mass spectra depending on the polymerisation conditions. These were used to analyse side reactions and gain information about the polymerisation process. The suggested formation of different chain ends is given below.

Formation of **1**— methoxy chain end

Methanol caps the oligomer chain ends in the quenching procedure and forms the methoxy chain end as shown in scheme 4-2. The relative intensity of the methoxy chain end indicates the fraction of living chain end left at the point of quenching. As mentioned above, at room temperature (21°C), no methoxy chain end is observed in the MALDI-TOF mass spectrum, which indicates that after 1 hour, no living chain ends are left. Lower polymerisation temperatures lead to a higher fraction of methoxy chain ends. Comparison of figure 4-2 and the MALDI-TOF mass spectrum of the -78°C reaction in figure 4-3 shows that that the added nucleophile, as well as the short polymerisation time largely increase the relative intensity of methoxy chain end, leading to a more controlled polymerisation.



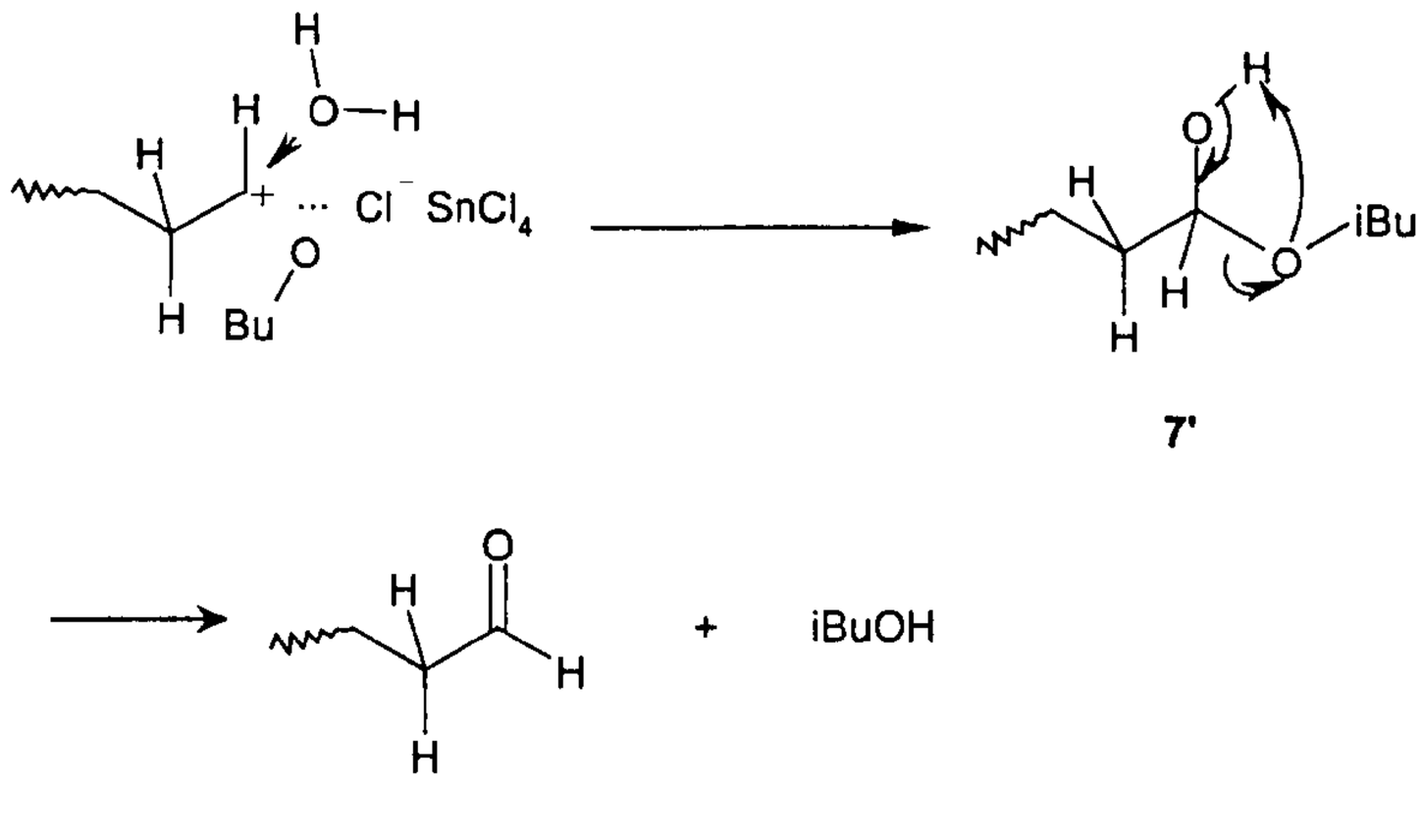
1

Scheme 4-2: Formation of methoxy chain end

Formation of **2** , **7** and **8**

According to Katayama [Katayama, 2001b], the formation of the aldehyde chain end is due to water capping of the carbocationic chain end. The proposed formation is shown in scheme 4-3. The observation of the first step product, **7**, on the same MALDI-TOF mass spectrum further proved the possibility of water capping. Release of isobutanol from **7** gives aldehyde chain end.

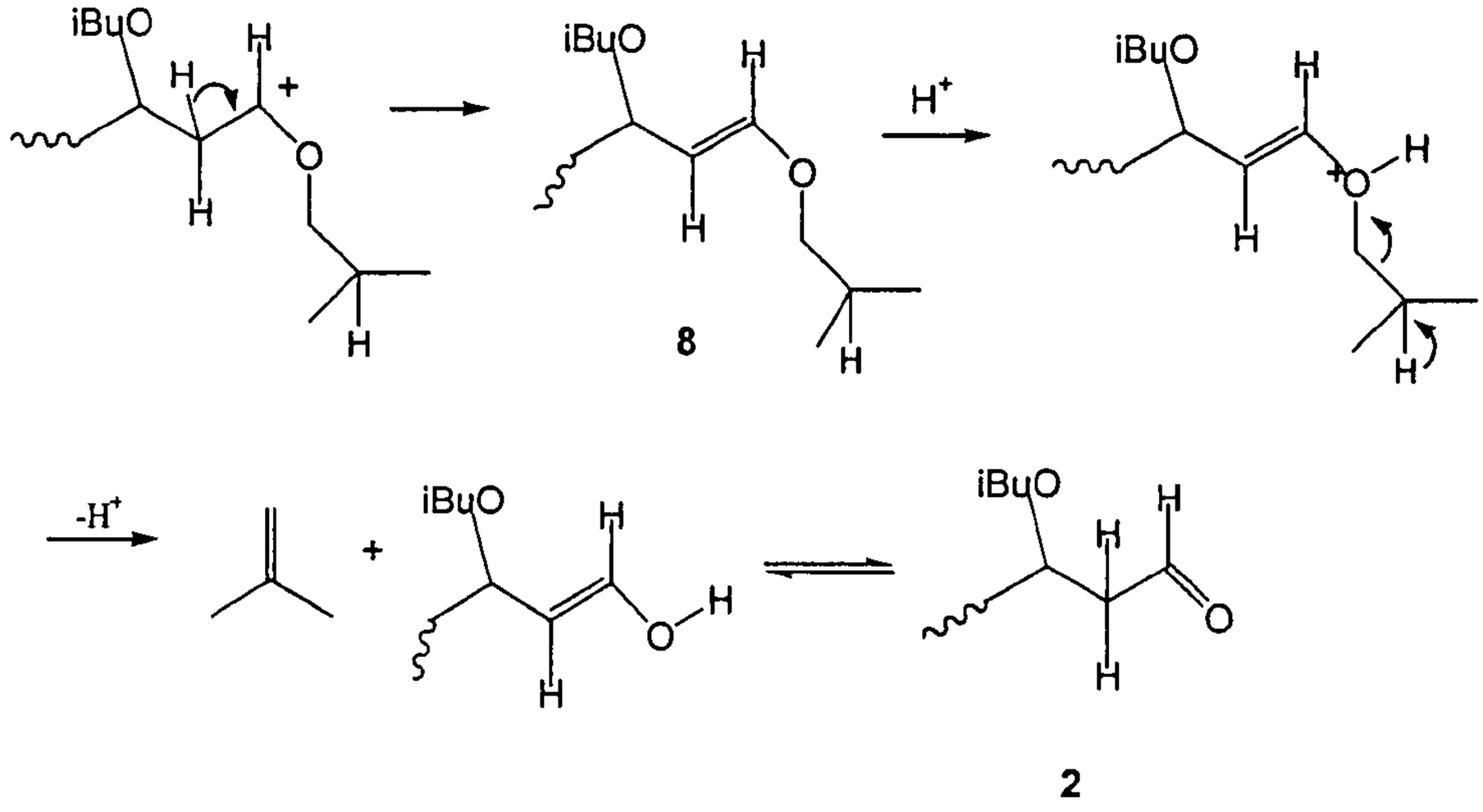
In accordance with the Japanese group's report, the aldehyde chain end can even form at -78° in the presence of *n*-Bu_4NCl, while other side reactions are largely reduced. Comparison of the MALDI-TOF mass spectra shows that the fraction of aldehyde chain end increases at -15°C.



Scheme 4-3: Formation of secondary alcohol and aldehyde chain ends as proposed by Katayama

Instead of water capping and the elimination of isobutanol from **7**, we have another proposal for the formation of the aldehyde chain end as shown in scheme 4-4. Elimination of a β-proton gives alkene chain end—compound **8**. It is considered that **2** can also be produced by elimination of 2-methylpropene from **8**.

Alkene chain end formation from chain transfer can be observed at all temperatures in the absence of a nucleophile. It is more predominant at room temperature and has a similar intensity at other polymerisation temperatures investigated.



Scheme 4-4: Formation of alkene and aldehyde chain ends

Formation of 4 and **5**

High concentration of Lewis acid could lead to more side reactions as shown in scheme 4-5. Firstly, β-elimination occurs between β-proton and the γ-isobutoxy groups, which leads to the release of isobutanol and the formation of the internal alkene oligomer chains with living chain ends. The presence of trace amounts of water or addition of methanol produced compounds **4** and **5**. A possible intermediate of the water capping is compound **9** but this cannot be proved by MALDI-TOF mass spectra. Addition of isobutanol could give compound **10**, as mentioned above also cannot be proved because of the overlap of the *m/z* value.

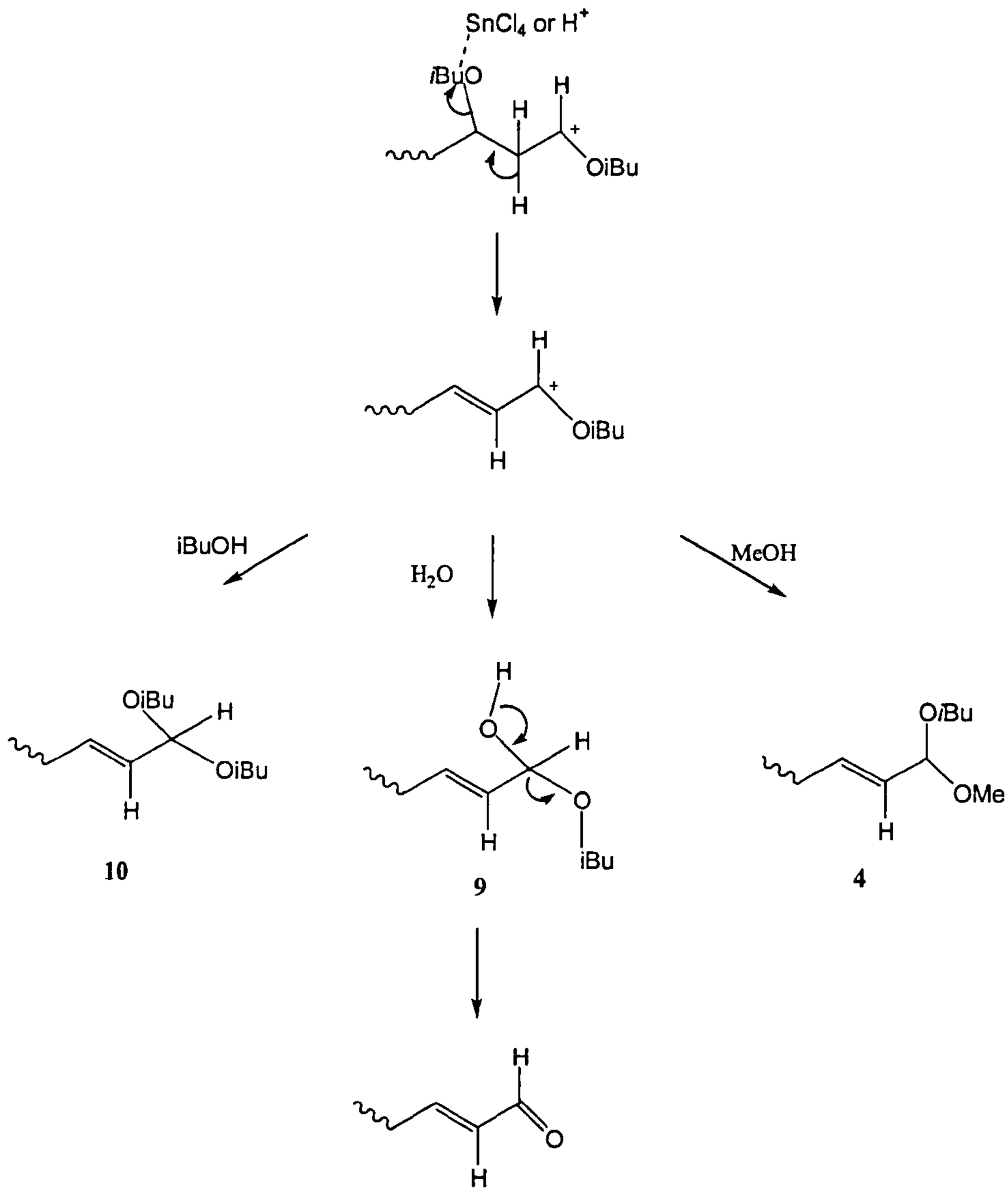
Although compounds **4** and **5** are observed in small amounts at all temperatures, like other oligomer chain ends from side reactions, they were not present at low polymerisation temperature in the presence of a nucleophile. At low temperature, the internal alkene aldehyde chain end is present in a higher amount than the internal alkene methoxy chain end.

The formation of **4** and **5** could also happen via the reaction shown in scheme 4-6. This indicates that β-elimination and the release of isobutanol occurs after the formation of the chain ends.

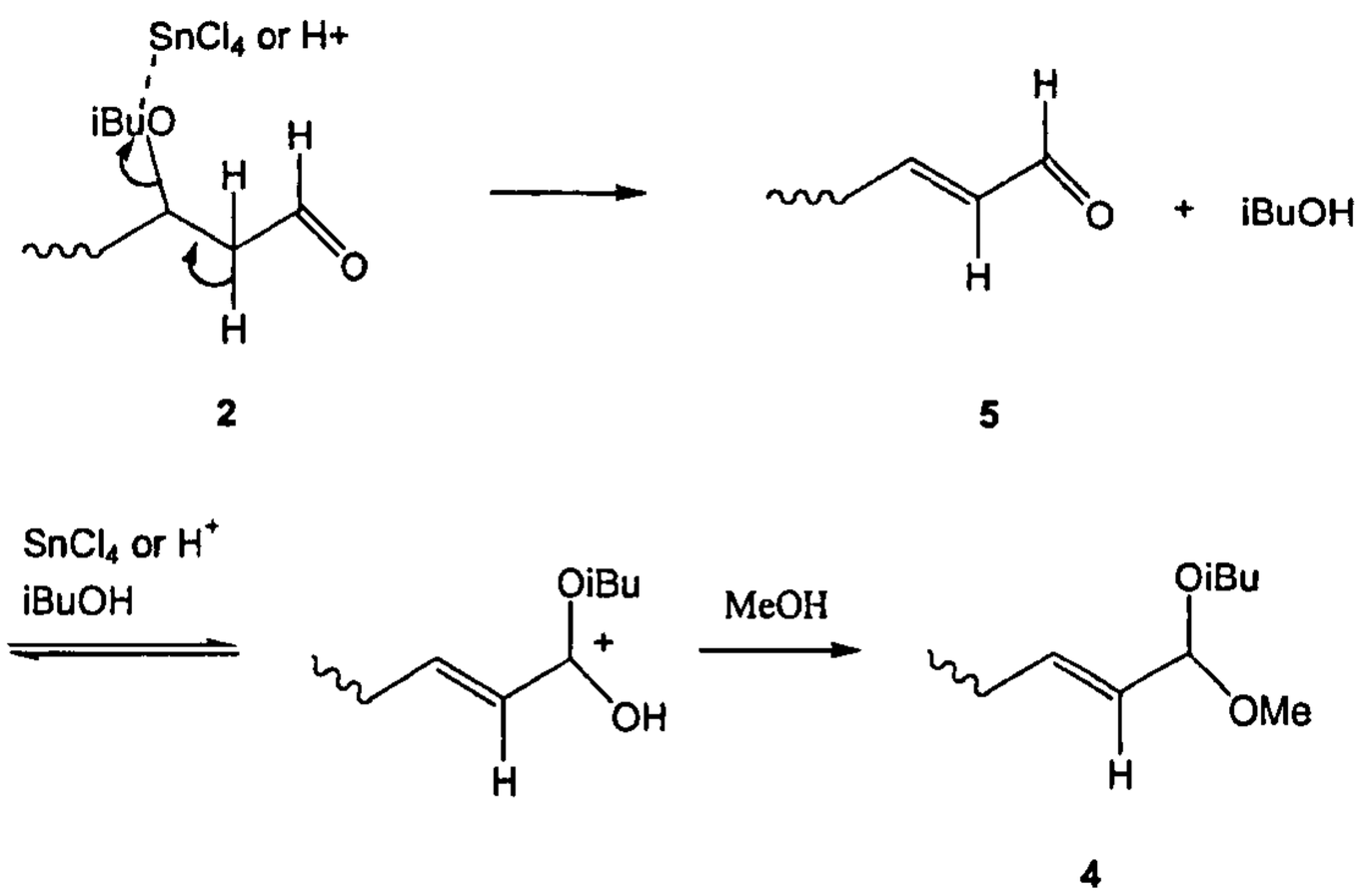
The observation of alkene, aldehyde and primary alcohol chain ends is accordance with one of the former reports. Lievens et al. reported the trimethylsilyl iodide and 1,1-diethoxyethane initiated polymerisation of octadecyl vinyl ether (ODVE) in the presence of ZnI_2 in toluene at 0°C. Alkenyl ether end groups formed by the transfer reaction become the same acetal end-groups as the active species when terminated with methanol during cationic polymerisation of ODVE [Lievens, 1996]. The formation of dioctadcyloxy acetal chain end indicates the formation of a octadecyloxy.

Formation of **6** and **7**

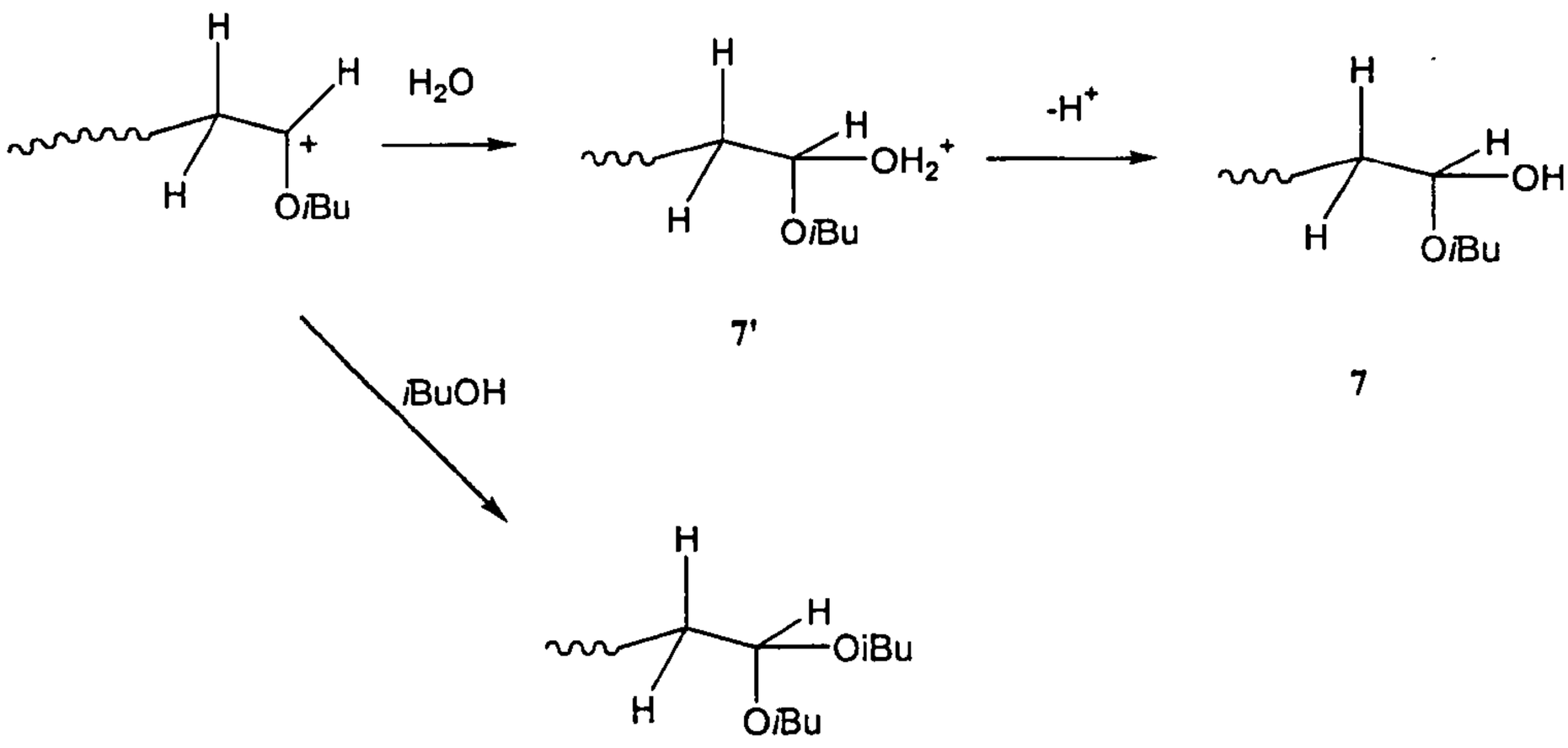
Scheme 4-7 shows the mechanism of formation of the secondary alcohol chain end— **7'** and **7**. Generally, proton ionisation (if observed at all) is much weaker than sodium ionisation for the same oligomer chain. The exception to this appeared here and this can be rationalised from the mechanism shown in scheme 4-7. According to our observation, proton ionisation of secondary alcohol chain ends is much stronger than sodium ionisation.



Scheme 4-5: Formation of internal alkene methoxy and internal alkene aldehyde chain ends



Scheme 4-6: Formation of internal alkene methoxy and internal alkene aldehyde chain end



Scheme 4-7: Formation of secondary alcohol and diisobutanol chain end

Generally side reactions are less prominent at lower polymerisation temperatures. Therefore the intensity of the peaks derived from different chain ends from side reactions also decreases. It is confusing to observe from figure 4-4 that this secondary alcohol chain end appeared to be stronger at lower temperatures. This observation can be explained by considering that **7'** is formed during the quenching procedure, i.e. the water present during the quenching procedure competes with methanol to cap the living chain end. When there are more living chain ends left at quenching (at low polymerisation temperature), a higher relative amount of **7'** and **7** is formed.

About the chain end **3**

Isobutanol formed from other side reactions caps the carbocationic chain end to produce the diisobutanol chain end as shown in scheme 4-7. Considering the fact that the intensity of the diisobutanol chain end is usually much stronger than that of the aldehyde and internal alkene oligomer chain ends, which produce isobutanol, there must be another side reaction that leads to the release of isobutanol. This is one of the reasons that the MALDI signal with the *m/z* of 100n+70 is postulated as the primary alcohol chain end **3** shown in figure 4-5. The formation of this relatively strong primary alcohol chain end results in the release of isobutanol which eventually caps the oligomer chain end and gives a stronger signal for the diisobutanol chain end. A reasonable mechanism for the formation of this primary alcohol chain end cannot

be given here. It is the predominant oligomer chain formed at room temperature and its intensity reduces when the polymerisation temperature decreases.

4.2.4 Discussion on the initiation system in general

The application of a new initiation system could indeed give a well-defined cationic polymerisation at low temperature (-78°C) with the presence of *n*-Bu_4NCl. A large amount of side reactions occur at all temperatures in the absence of nucleophiles. Side reactions observed were mainly due to water capping, β-proton elimination and isobutanol capping, or a combination of these. Generally, low temperature and the addition of nucleophiles help to reduce the side reactions.

At room temperature the primary alcohol chain end becomes dominant. At 0°C the diisobutanol chain end becomes prominent, indicating that the polymerisation temperature favors the formation of isobutanol and/or the isobutanol capping, which occurs before the termination. This is in accordance with the explanation that the secondary alcohol chain end is probably formed at the quenching stage. The lower polymerisation temperature tends to result in the survival of more carbocationic chains at the end of the polymerisation (and this leads to more methoxy chain ends). The use of low temperature could also reduce the formation of the diisobutanol chain end, although it is not clear exactly which step of the side reaction was suppressed, the formation of isobutanol or the capping of isobutanol to the chain end.

4.3 *Ab initio* chain end functionalisation

4.3.1 A*b initio* end-capping by silyl enol ethers

SEE 1, **2**, **3**, and **4** in figure 4-1 successfully capped the oligomer chain and chain end functionalities were obtained using this initiation system. End-capping with **SEE 5** and **SEE 6** appeared not to be effective because chain end functionalities were not found using either NMR or MALDI-TOF MS analysis, instead the methoxy chain end and other chain ends from the side reactions were observed when **SEE 5** and **6** were used.

The ^1H NMR spectrum, with assignments, of a polymerisation carried out in the absence of silyl enol ether is shown in figure 4-6. Two expanded regions of the spectrum show the detailed resonances 1 and 8. Clearly the tertiary proton 7 is located around 4.6 ppm as a broad resonance. The ω-end methyl resonance 8 is found

around 3.27 ppm as a doublet. The α-end methyl resonance is located at 1.1 as a doublet. Assignments 2 to 6 correspond to the broad main chain proton resonances. The aldehyde proton resonance can be found downfield at 9.7 ppm, and this is in accordance with MALDI-TOF MS analysis of the same sample shown in figure 4-2.

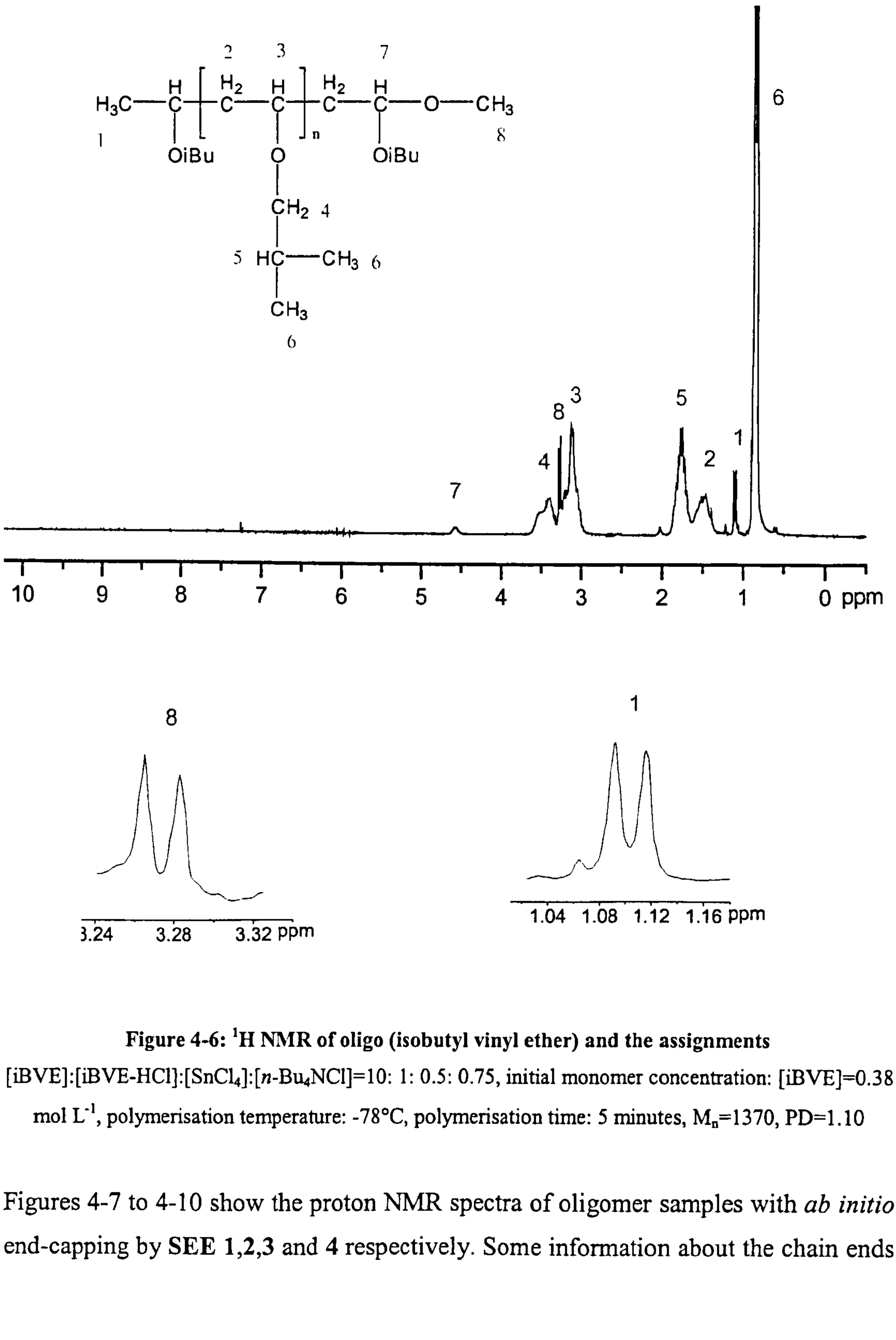


Figure 4-6: ^{1}H NMR of oligo (isobutyl vinyl ether) and the assignments

[iBVE]:[iBVE-HCl]:[$SnCl_4$]:[*n*-Bu_4NCl]=10: 1: 0.5: 0.75, initial monomer concentration: [iBVE]=0.38 mol L^{-1}, polymerisation temperature: -78°C, polymerisation time: 5 minutes, M_n=1370, PD=1.10

Figures 4-7 to 4-10 show the proton NMR spectra of oligomer samples with *ab initio* end-capping by **SEE 1,2,3** and **4** respectively. Some information about the chain ends

can be extracted from these figures. The common observation from figures 4-7, 4-8 and 4-9 is the reduction or disappearance of signal 7, the ω-end tertiary proton resonance around 4.6 ppm. A new broad resonance around 4.0 ppm, presented as signal 9, which is due to the functionalised ω-end tertiary proton resonance, appeared in these spectra. The microelectron environment variance of this tertiary proton led to this up field shift from 4.6 ppm to 4.0 ppm.

Also the doublet at 3.27 ppm is significantly reduced in the NMR spectrum of the functionalised oligomer samples; figures 4-7, 4-8, 4-9 and 4-10 indicate the reduction of methoxy chain ends in these samples. The ω-end group methylene proton resonance, labeled as 10, is also observed in some instances.

The aromatic resonances shown in figure 4-7 and 4-8 indicate the presence of the phenyl and 4-methoxy phenyl groups in the oligomer samples. The integration of these aromatic resonances, together with the integrations of α-end methyl resonances at 1.1 ppm can be used to calculate the oligomer's average chain end functionalities when **SEE 1** and **SEE 2** are applied in end-capping. As shown in figure 4-7, there is a small amount of acetophenone in the oligomer sample. Although the phenyl resonance of acetophenone coincides with the resonance for the phenyl group resonance attached to the oligomer chain end, the methyl group resonance α to the ketone appears at 2.6 ppm as assignment 14 indicates the presence of a small amount of acetophenone, the desilylation product of **SEE 1**. The amount of acetophenone is negligible and the main intensity of the aromatic resonance is due to the phenyl group attached to oligomer chain end.

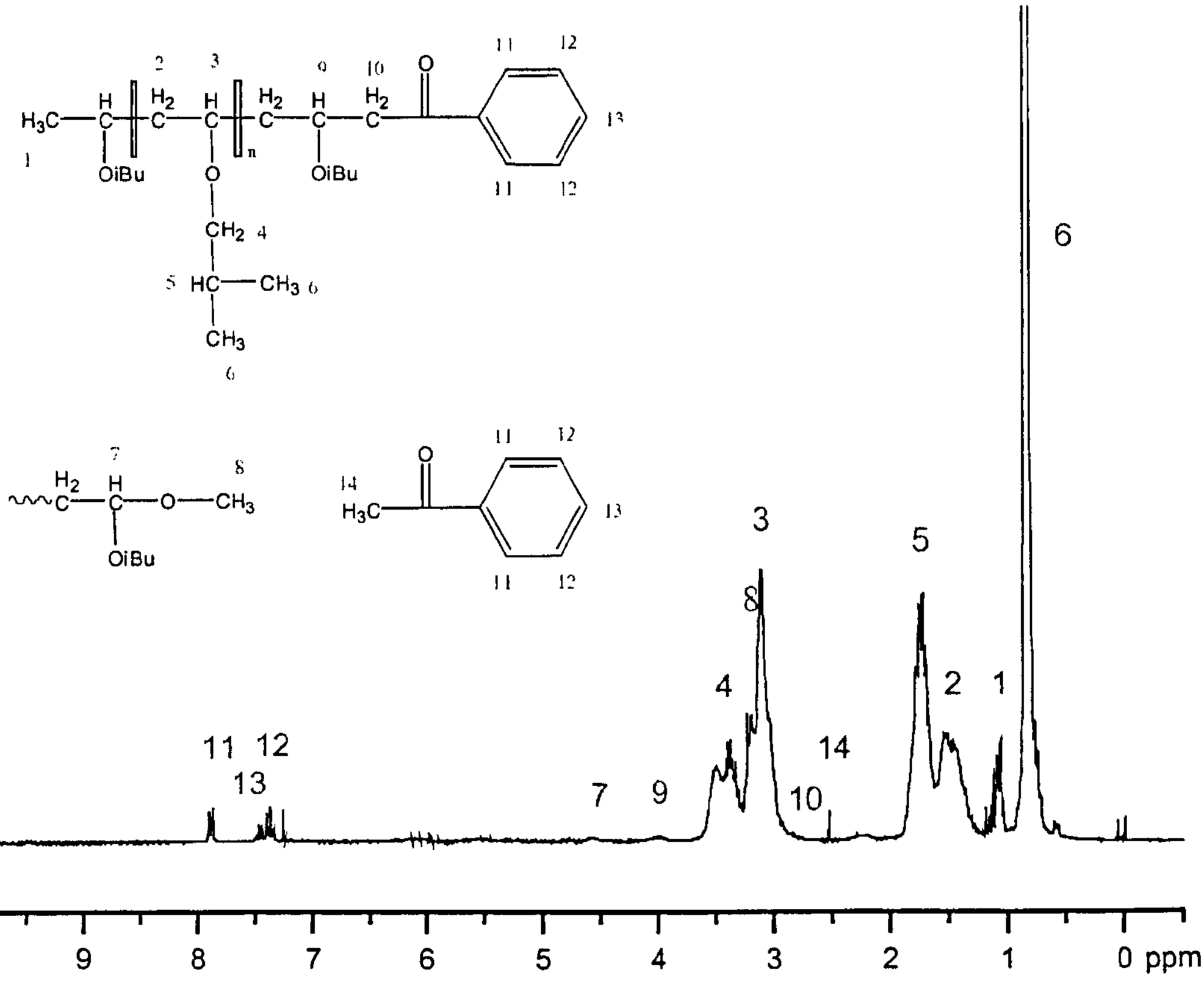


Figure 4-7: ^{1}H NMR of Oligo (isobutyl vinyl ether) with *ab initio* chain end functionalisation with SEE 1

[iBVE]:[iBVE-HCl]: [SEE 1]: [$SnCl_4$]=10: 1: 1: 0.5, initial monomer concentration: [iBVE]=0.38 mol L^{-1}, polymerisation temperature: -15°C, polymerisation time: 60 minutes, M_n=960, PD=2.45, Fn=69.7%, Monomer conversion: 75.2%

This desilylation product also exists when **SEE 2** is applied in end-capping as shown in figure 4-8. Signals 14 and 17 should have the same intensity as the resonance for 4-methoxyacetophenone. The non-proportional signals 14 and 17 indicate that only a small amount of 4-methoxyacetophenone is left in the sample and the majority of the resonance 17 is due to the functionalised ω-end group. Disappearance of the aldehyde proton resonance and the ω-end tertiary proton 7 both indicate a high degree of end-capping and that other side reaction chain ends have been suppressed.

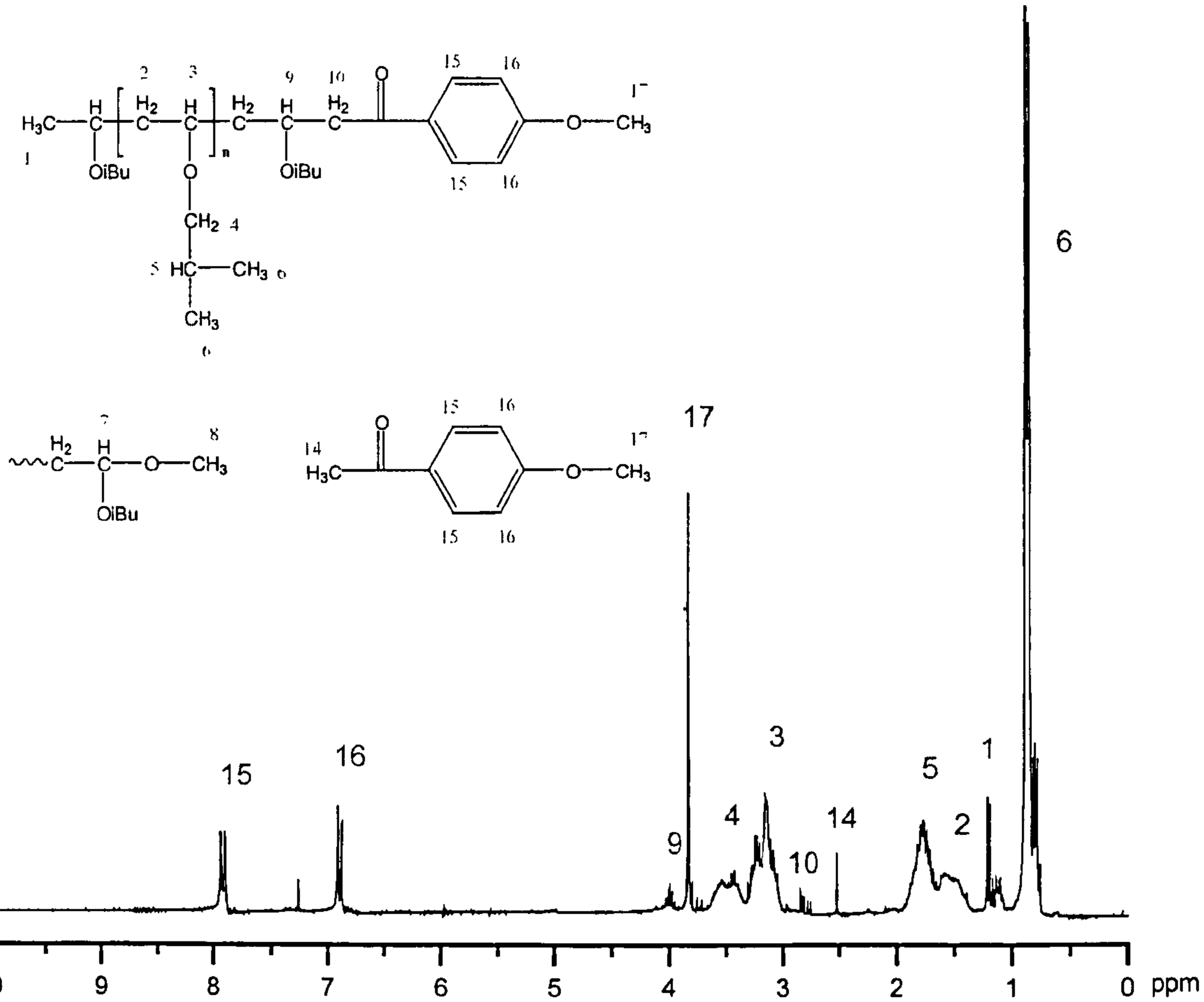


Figure 4-8: ^{1}H NMR of Oligo (isobutyl vinyl ether) with *ab initio* chain end functionalisation with SEE 2

[iBVE]:[iBVE-HCl]: [SEE 2][$SnCl_4$]: [*n*-Bu_4NCl] =10: 1: 1: 0.5: 0.75, initial monomer concentration: [iBVE]=0.38 mol L^{-1}, polymerisation temperature: -15°C, polymerisation time: 60 minutes, M_n=650, PD=8.09, Fn=95.9%, Monomer conversion: 90.6%

The aldehyde proton resonance is also absent when **SEE 3** is applied in end-capping (figure 4-9). An up field shift of the tertiary ω-end proton from 4.6 ppm to 4.0 ppm is also observed. As discussed in the former chapter, the ω-end methyl resonances overlaps with the α-end methyl resonance and a much stronger signal around 1.1 ppm is observed. C-H correlation NMR helped to separate the overlapped chain end signals based on the fact that they are attached to different carbons. A C-H correlation NMR spectrum is presented in a separate section.

Again, the α-methyl resonance from 3,3-dimethyl butan-2-one 19 is around 2.1 ppm, indicating the presence of tiny amount of a small molecule as the desilylation product of **SEE 3**.

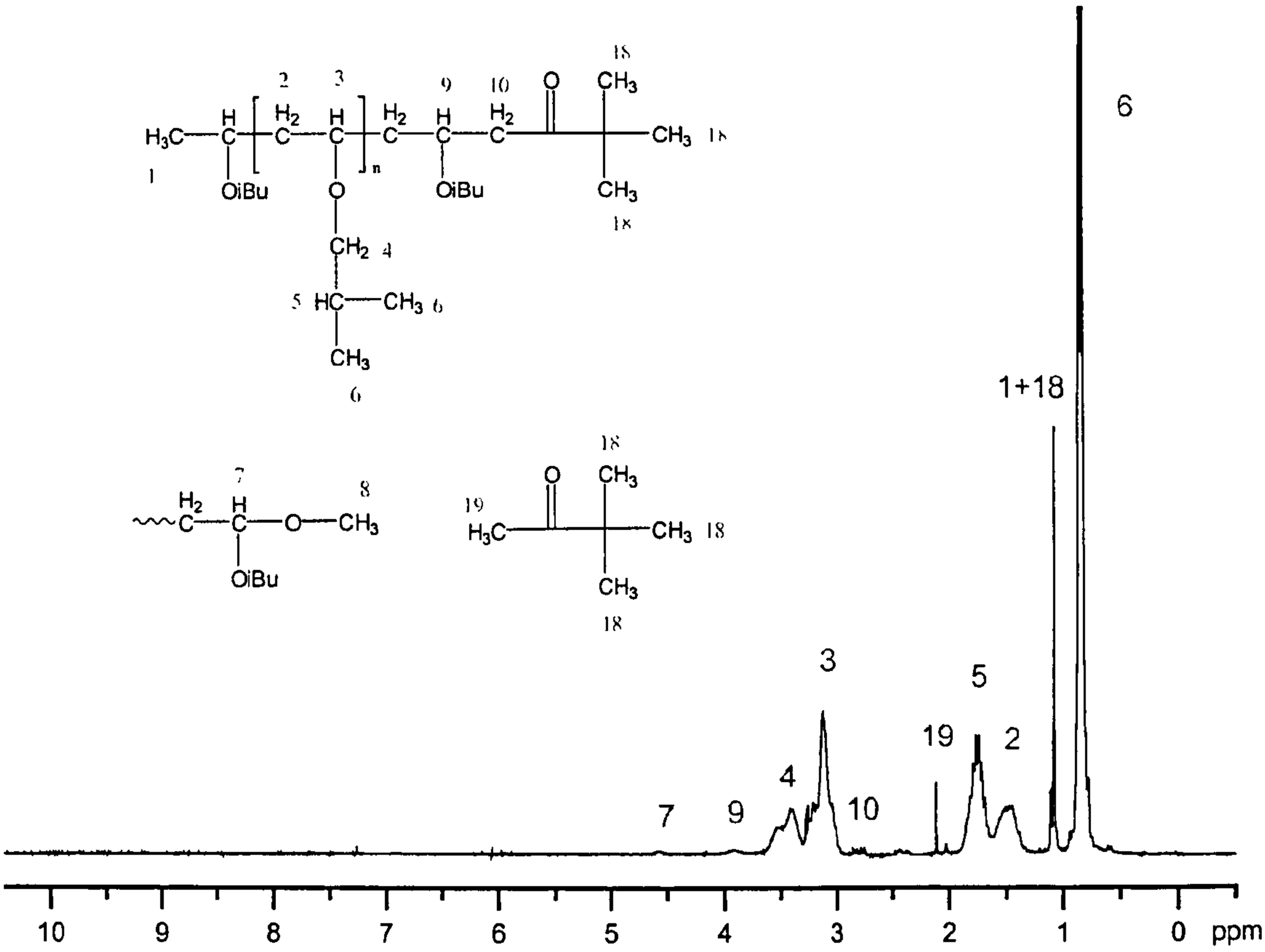


Figure 4-9: ^1H NMR of Oligo (isobutyl vinyl ether) with *ab initio* chain end functionalisation with

SEE 3

[iBVE]:[iBVE-HCl]: [SEE 3]:[$SnCl_4$]: [*n*-Bu_4NCl] =10: 1: 2: 0.5: 0.75, initial monomer concentration: [iBVE]=0.38 mol L^{-1}, polymerisation temperature: -78°C, polymerisation time: 5 minutes, M_n=1610, PD=1.14, Fn=48.4%, Monomer conversion: 90.9%

SEE 4 gives an ester chain end after end-capping. It can been seen from figure 4-10 that the aldehyde resonance and a considerable signal 7 are still present in the NMR spectrum of the oligomer indicating a low degree of end-capping. As a result of the overlapped resonance, it is difficult to determine whether the new signals, 20 and 21, are from the oligomer chain end or the desilylation product.

The ω-end methoxy resonance, if it exists, is not comparably strong as the signal 7 indicating the presence of some other chain end with the same ω-end tertiary proton resonance. It could be the diisobutanol chain end.

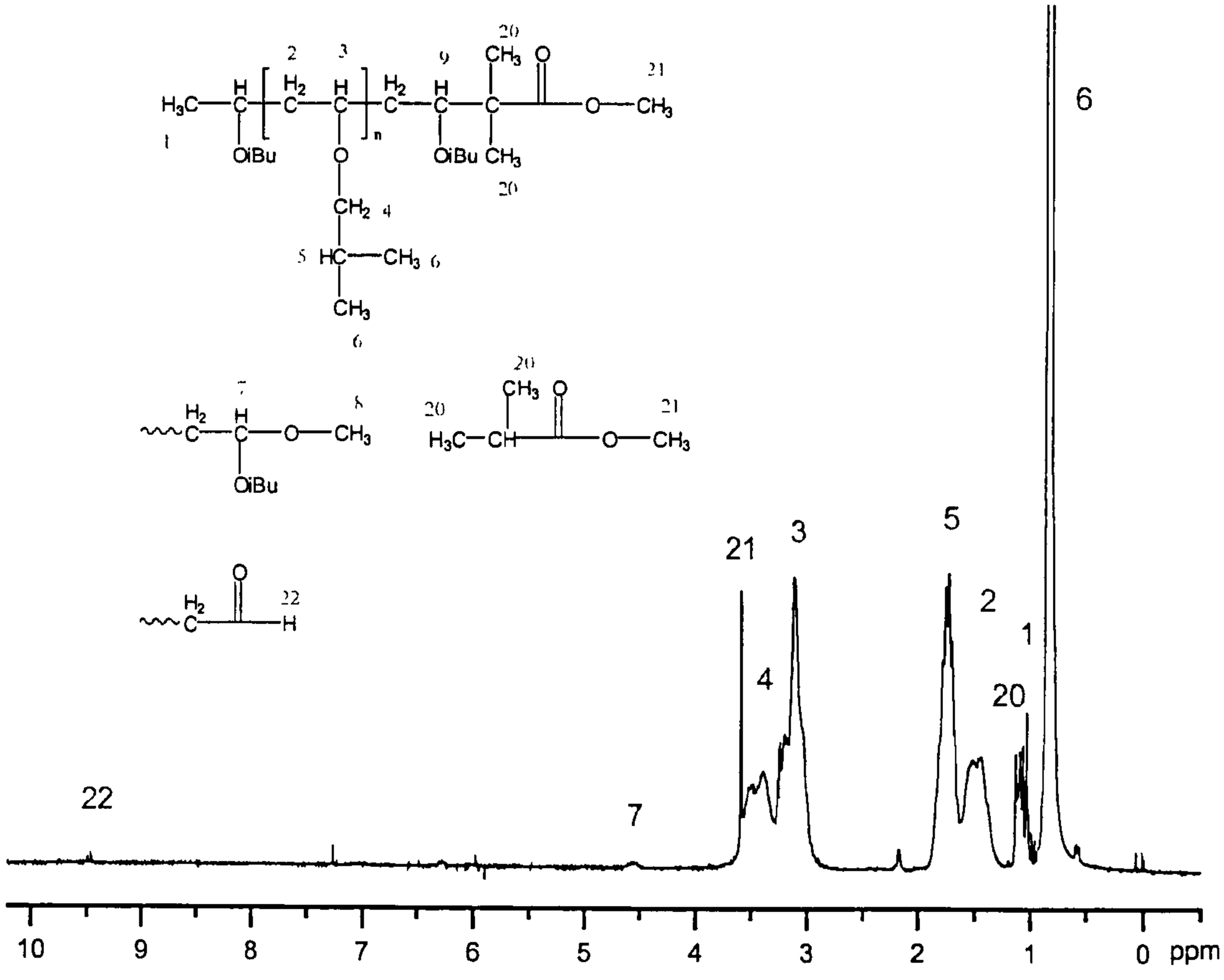


Figure 4-10: ^1H NMR of Oligo (isobutyl vinyl ether) with *ab initio* chain end functionalisation with SEE 4

[iBVE]:[iBVE-HCl]: [SEE 4]: [$SnCl_4$] =10: 1: 1: 0.5, initial monomer concentration: [iBVE]=0.38 mol L^{-1}, polymerisation temperature: -78°C, polymerisation time: 60 minutes, M_n=1210, PD=2.20, Monomer conversion: 100%

It can be seen from these NMR spectra that **SEE 1, 2** and **3** are attached to the oligomer chain with good chain end functionalities using the current polymerisation system.

Among the unfunctionalisedd chain ends, only the aldehyde and methoxy chain ends can be observed in the NMR spectra. Other side reactions still occurring in the *ab initio* chain end functionalisation during the polymerisations are difficult to detect because of the weak resonance of these chain ends as well as the overlapping of the signals. For example, the presence of the diisobutanol chain end is impossible to prove by NMR spectroscopy, but the MALDI-TOF spectrum will provide useful information.

Figure 4-11 shows the combined MALDI-TOF spectra of OiBVEs end-capped by silyl enol ether **1**, **2**, **3** and **4** respectively. The samples applied are the same as the 4 NMR spectra above. The strongest oligomer series on each spectrum (figure 4-11) is due to the corresponding silyl enol ether functionalised OiBVE chain end. Side reaction chain ends are substantially decreased in the presence of silyl enol ethers. It can be seen that the chain end functionalities are high, especially for **SEE 1** and **SEE 2**. The **SEE 3** functionalised oligomer contains two series of oligomer chains, the main series is the **SEE 3** capped OiBVE. The second series apparent at higher mass with relatively low intensity is the OiBVE with the methoxy chain end.

Detailed information on the oligomer chain ends is presented in figure 4-12. Various chain ends are labeled in figure 4-12 and the structures of the various silyl enol ether functionalisedd oligomer are listed in table 4-3 with the theoretical *m/z* values and the observed values. 10 out of 11 oligomers listed in table 4-3 are observed although not all of them are presented in figure 4-12. The differences between the theoretical and the observed values are generally within 0.4 Daltons out of 1k Daltons (i.e. accurate to within 0.04%).

Table 4-3: MALDI-TOF MS observations on OiBVEs end-capped by silyl enol ethers

number	SEE	OiBVE with different ω-ends	OiBVE *m/z*	
			Theore.	Experi.
1-1	1	H-$(iBVE)_{10}$-CH_2-C(=O)-Ph/Na^+	1143.9	1144.3
1-2	1	H-$(iBVE)_{10}$-CH_2-CH=CH-C(=O)-Ph/Na^+	1170.0	1170.2
1-3	1	H-$(iBVE)_{10}$-CH_2-CH(OH)-CH_2-C(=O)-Ph/Na^+	1087.9	1088.2
2-1	2	H-$(iBVE)_{10}$-CH_2-C(=O)-Ph-O-Me/Na^+	1174.0	1174.3
2-2	2	H-$(iBVE)_{10}$-CH_2-CH=CH-C(=O)-Ph-O-Me/Na^+	1200.0	1200.2
2-3	2	H- $(iBVE)_{10}$-CH_2-CH(OH)-CH_2-C(=O)-Ph-OMe/Na^+	1218.0	1218.3
3-1	3	H-$(iBVE)_{10}$-CH_2-C(=O)-$C(CH_3)_3$/Na^+	1124.0	1124.2
3-2	3	H-$(iBVE)_{10}$-CH_2-CH=CH-C(=O)-$C(CH_3)_3$/Na^+	1150.0	1150.3
3-3	3	H-$(iBVE)_{10}$-CH_2-CH(OH)CH_2-C(=O)-$C(CH_3)_3$/Na^+	1168.0	-
3-4	3	H-$(iBVE)_{10}$-CH_2-CH(OH)CH_2-C(=O)-$C(CH_3)_3$/H^+	1146.0	1146.5
4-1	4	H-$(iBVE)_{10}$-CH_2-$COOCH_3$/Na^+	1126.0	1126.4
4-2	4	H-$(iBVE)_{10}$-CH=CH$C(CH_3)_2$-$COOCH_3$/Na^+	1152.0	1152.5

Monoisotope oligomer ion mass was calculated for theoretical value and picked up for experimental value.

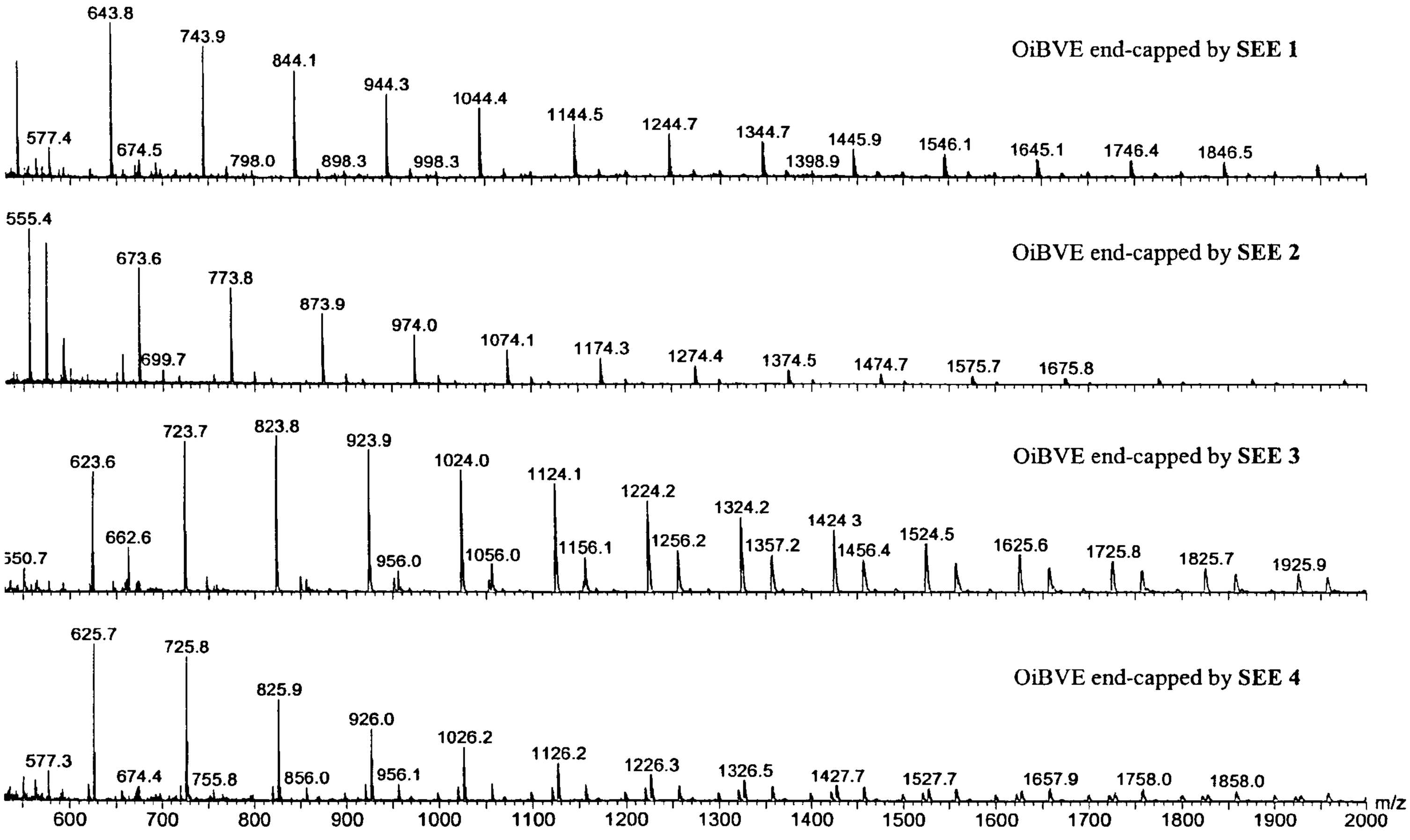


Figure 4-11: MALDI-TOF mass spectra of OiBVEs end-capped by different silyl enol ethers

[iBVE]=0.38mol L^{-1}, [iBVE]:[iBVE-HCl]· [**SEE 1**]· [$SnCl_4$]=10: 1: 1: 0.5, polymerisation temperature: -15°C, polymerisation time· 60 minutes, M_n=960, PD=2.45, Fn=69.7%, Monomer conversion· 75.2%
[iBVE].[iBVE-HCl]: [**SEE 2**][$SnCl_4$]· [*n*-Bu_4NCl] =10: 1: 1: 0.5: 0.75, polymerisation temperature: -15°C, polymerisation time: 60 minutes, M_n=650, PD=8 09, Fn=95 9%, Monomer conversion· 90.6%
[iBVE].[iBVE-HCl]: [**SEE 3**]:[$SnCl_4$]· [*n*-Bu_4NCl] =10: 1: 2: 0.5. 0.75, polymerisation temperature -78°C, polymerisation time· 5 minutes, M_n=1610, PD=1.14, Fn=48.4%, Monomer conversion. 90.9%
[iBVE]:[iBVE-HCl]. [**SEE 4**]: [$SnCl_4$] =10: 1: 1· 0.5, polymerisation temperature: -78°C, polymerisation time. 60 minutes, M_n=1210, PD=2 20, Monomer conversion: 100%

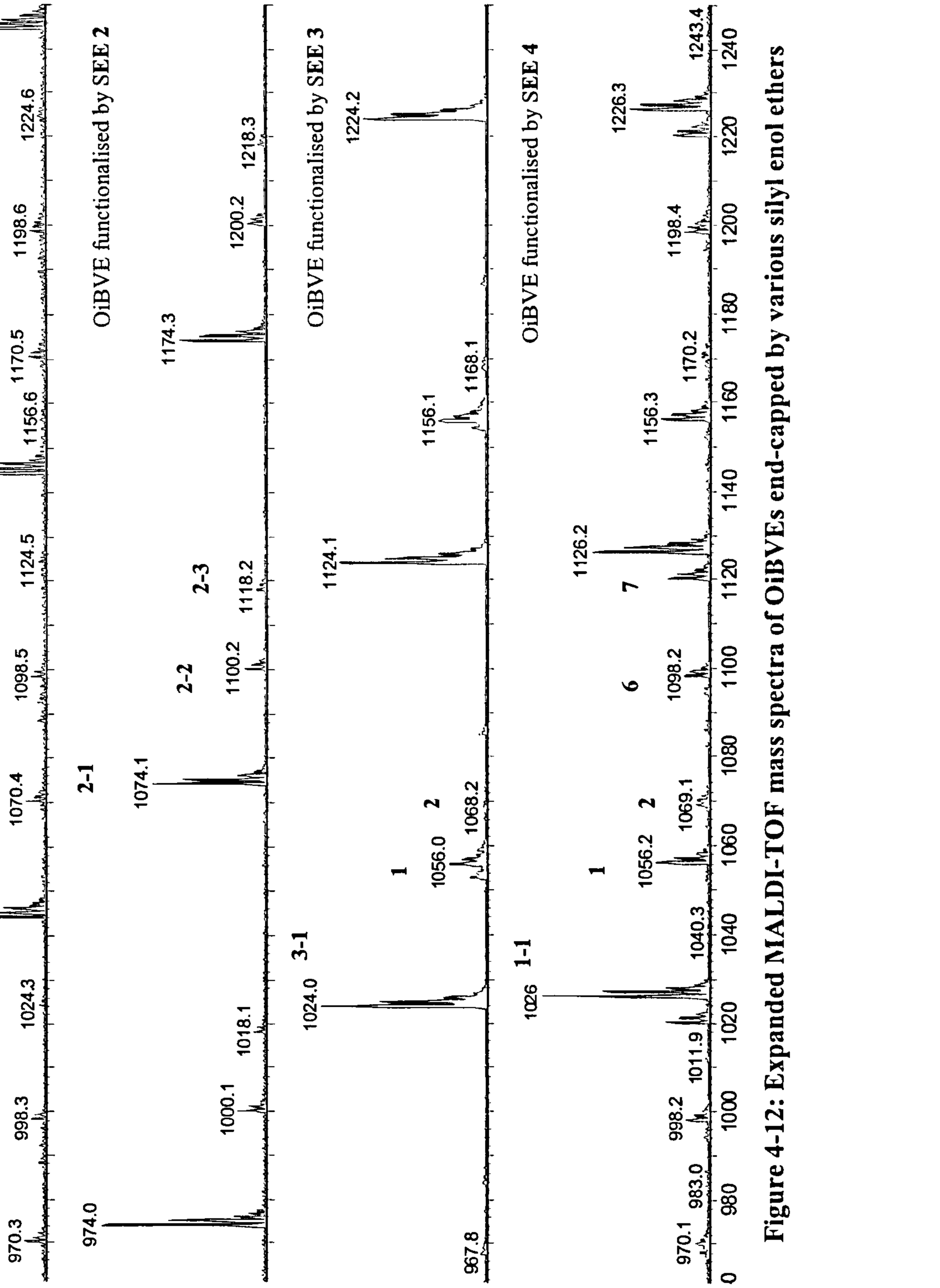


Figure 4-12: Expanded MALDI-TOF mass spectra of OiBVEs end-capped by various silyl enol ethers

There is more variation in the chain end functionalities in the higher molecular weight range. To give a full overview of the variances, figure 4-13 shows the high mass MALDI-TOF mass spectra of figure 4-11. Although the amount of oligomer with higher molecular weight is not high, the spectra contain slightly different information compared to figure 4-12.

It can be seen from figure 4-13 that for SEE **1**, chain end functionalities are still high at higher mass, although there is a slightly higher amount of diisobutanol chain end. For **SEE 2** there is still very little side reaction chain end presents at this mass range. All three of the oligomer series presented are **SEE 2** functionalised OiBVE. For **SEE 3** there is higher amount of methoxy chain end apparent at this higher mass range compared with the lower mass range. **SEE 4** functionalised OiBVE is no longer prominent at this higher mass range. A large amount of methoxy chain end and other side reactions chain ends are present, even under less strictly controlled cationic polymerisation conditions, the effects of *ab initio* end-capping of silyl enol ethers were still promising.

4.3.2 The suppression of side reactions by end-capping of silyl enol ethers

In addition to the high chain end functionalities obtained, figures 4-11 to 4-13 indicate that chain ends from side reactions are largely reduced in the *ab initio* chain end functionalisation.

Figure 4-12 illustrates that among the relatively low molecular weight range, only a small amount of diisobutanol, alkene and possibly primary alcohol chain ends were left in the presence of **SEE 1**. No side chain ends due to side reactions were found in the presence of **SEE 2**. The methoxy chain end was found in the oligomer samples when **SEE 3** was applied, indicating that a small amount oligomer chain ends were not capped by **SEE 3** (i.e. they were left living at quenching).

It was observed that more side reactions occurred when **SEE 4** was applied in end-capping. Oligomers with end groups **2**, **6** and **7'** from side reactions were found in slightly higher amount, as well as higher amount of methoxy chain ends, indicating a relatively low end-capping reactivity of **SEE 4**.

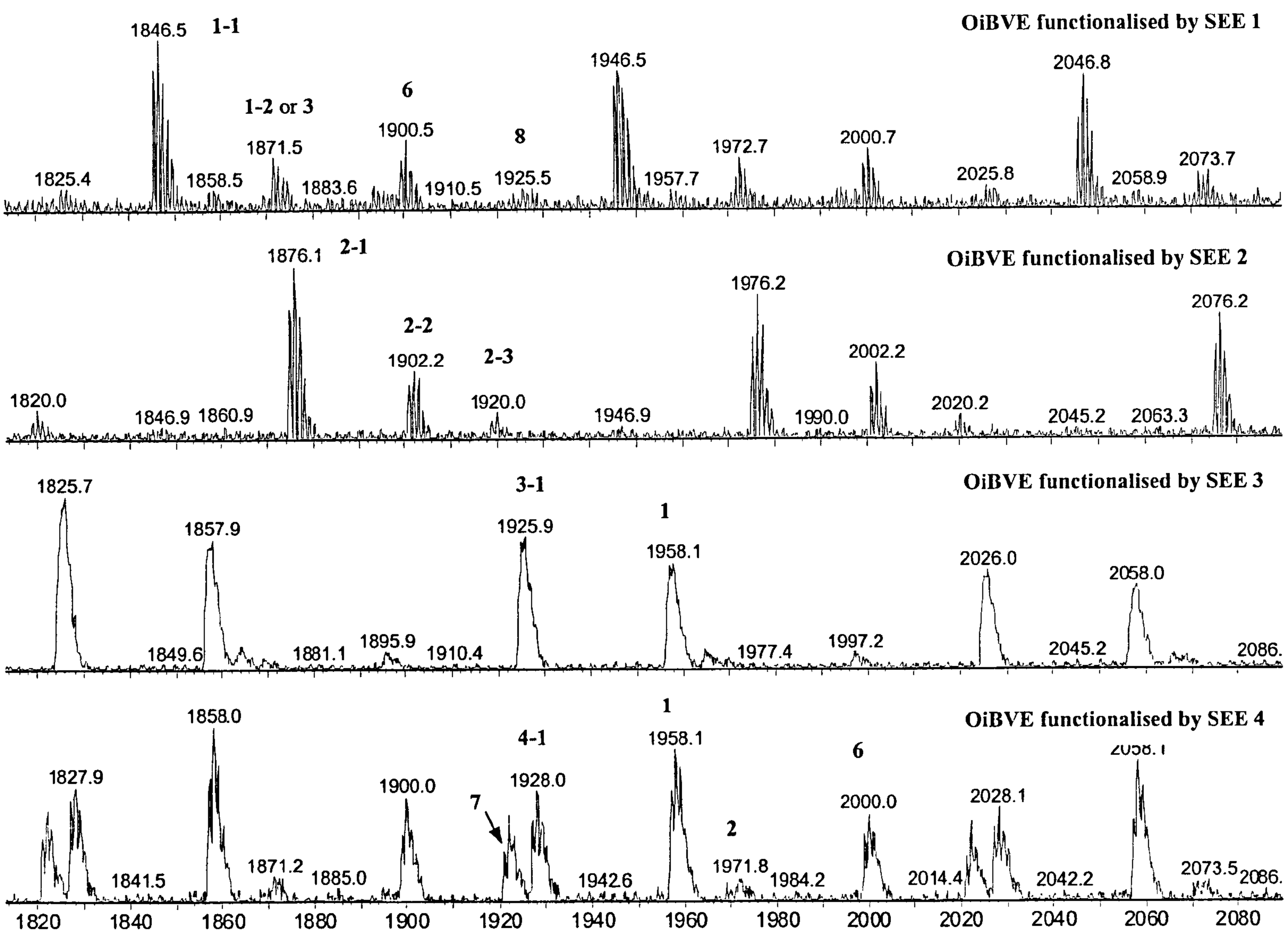


Figure 4-13: Expanded MALDI-TOF mass spectra of functionalised OiBVE at higher mass

Oligomers presented in figure 4-11 to figure 4-13 were prepared under different conditions. The results obtained would be more meaningful if the polymerisation conditions were kept the same and the side reactions were still suppressed. Figure 4-14 shows MALDI-TOF mass spectra of OiBVEs from the parallel polymerisations.

Even at this low temperature of -78°C, side reactions still occurred. A large amount of diisobutanol chain end **6** and secondary alcohol chain end **7'** were formed, as well as the methoxy chain end **1** (formed during quenching). Prominent functionalised chain ends were produced when silyl enol ethers were applied in the end-capping, therefore indicating that the four silyl enol ethers are highly active. End-capping largely suppressed side reactions in the polymerisation and produced high chain end functionalities.

Cationic polymerisation is usually performed at low temperature to reduce side reactions and ambient temperature is not often a choice for investigation. For a feasible application the exploration of *ab initio* studies on chain end functionalisation confirms the ambient temperature of polymerisation. Figure 4-15 shows 5 MALDI-TOF mass spectra of OiBVEs from parallel polymerisations at 21°C. **SEE 1**, **2** and **3** still give the functionalised oligomer chains as the dominant species and application of **SEE 4** also produces the functionalised chains as the main series. This is an exciting result about the end-capping i.e. under ambient temperature and in the absence of added salt, side reactions are largely reduced and chain end functionalities obtained are high in cationic oligomerisation.

It is clear that in the polymerisation system, where large amounts of side reactions occur at all temperatures in the absence of added nucleophile. However, in the presence of reactive silyl enol ethers, the side reactions observed are largely reduced and high chain end functionalities are obtained. This indicates that the end-capping rate is higher than many of the side reactions that lead to diisobutanol and alcohol chain ends i.e. end-capping has a higher rate than water capping or isobutanol capping. So that although water still exists in the system, its influence has been suppressed. When the active silyl enol ethers were consumed, concentration of living chain ends also decreased and this also leads to the observed reduction in water-capping or isobutanol capping.

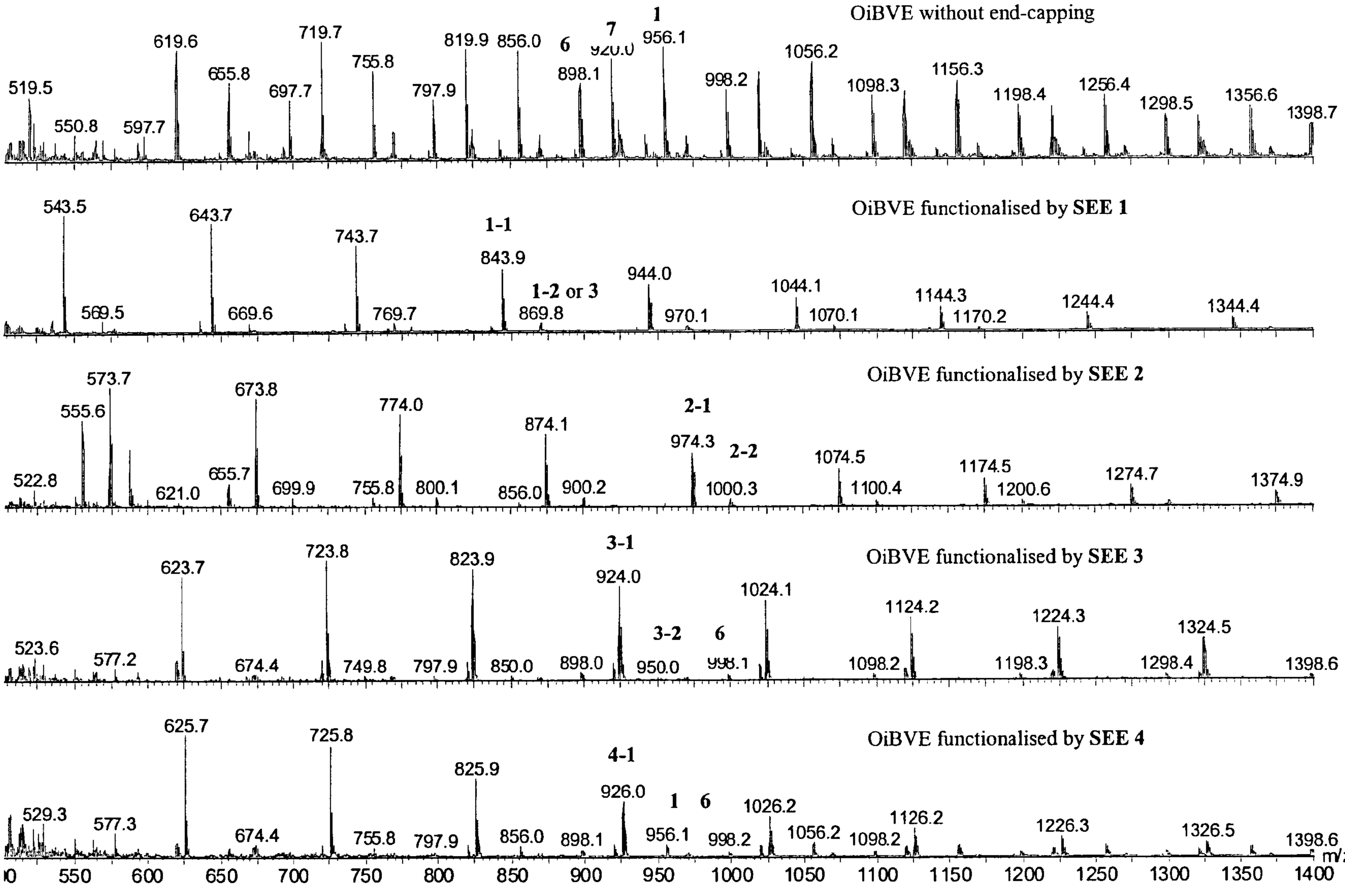


Figure 4-14: Suppression of side reactions by end-capping with silyl enol ethers in the parallel polymerisation at -78°C

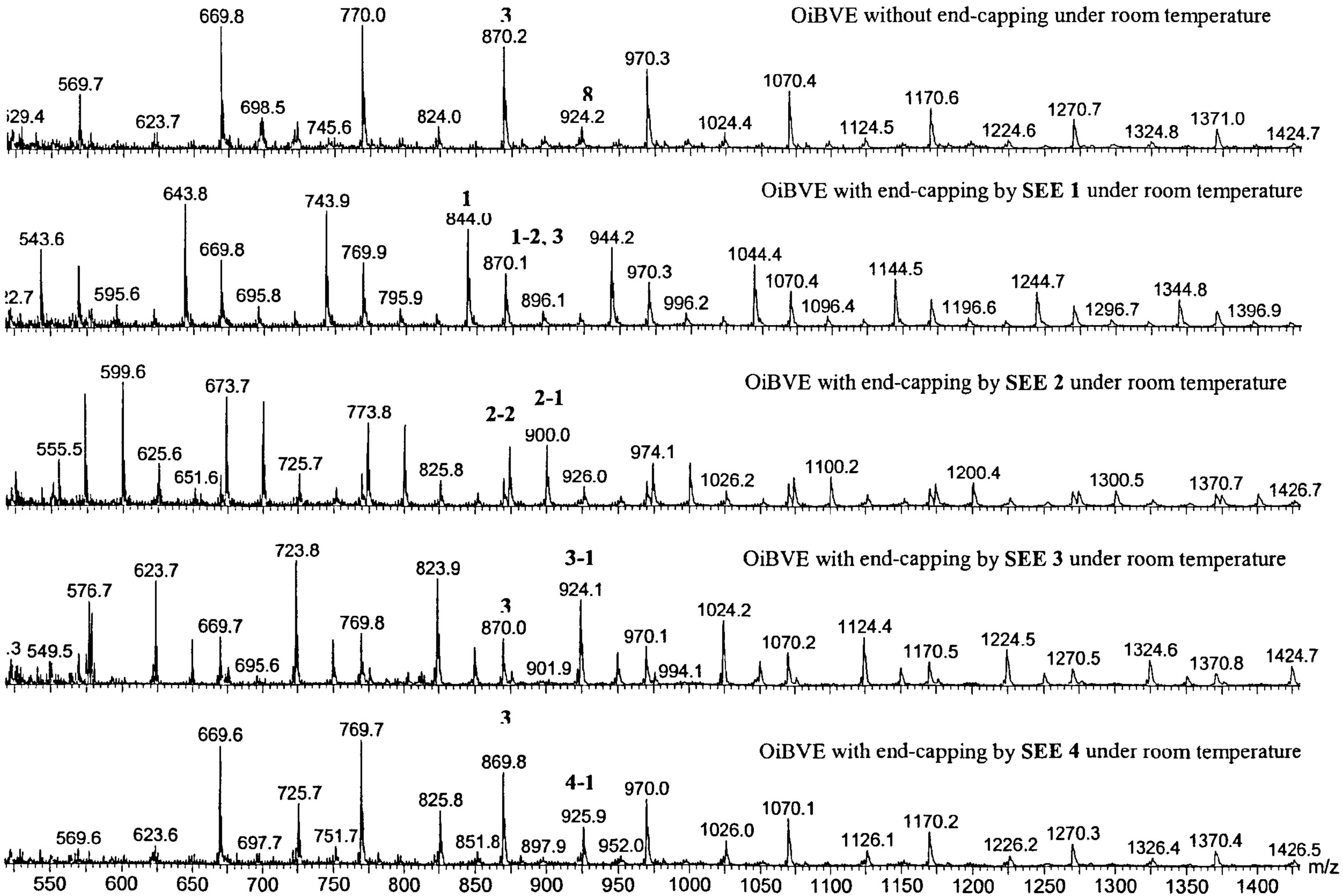


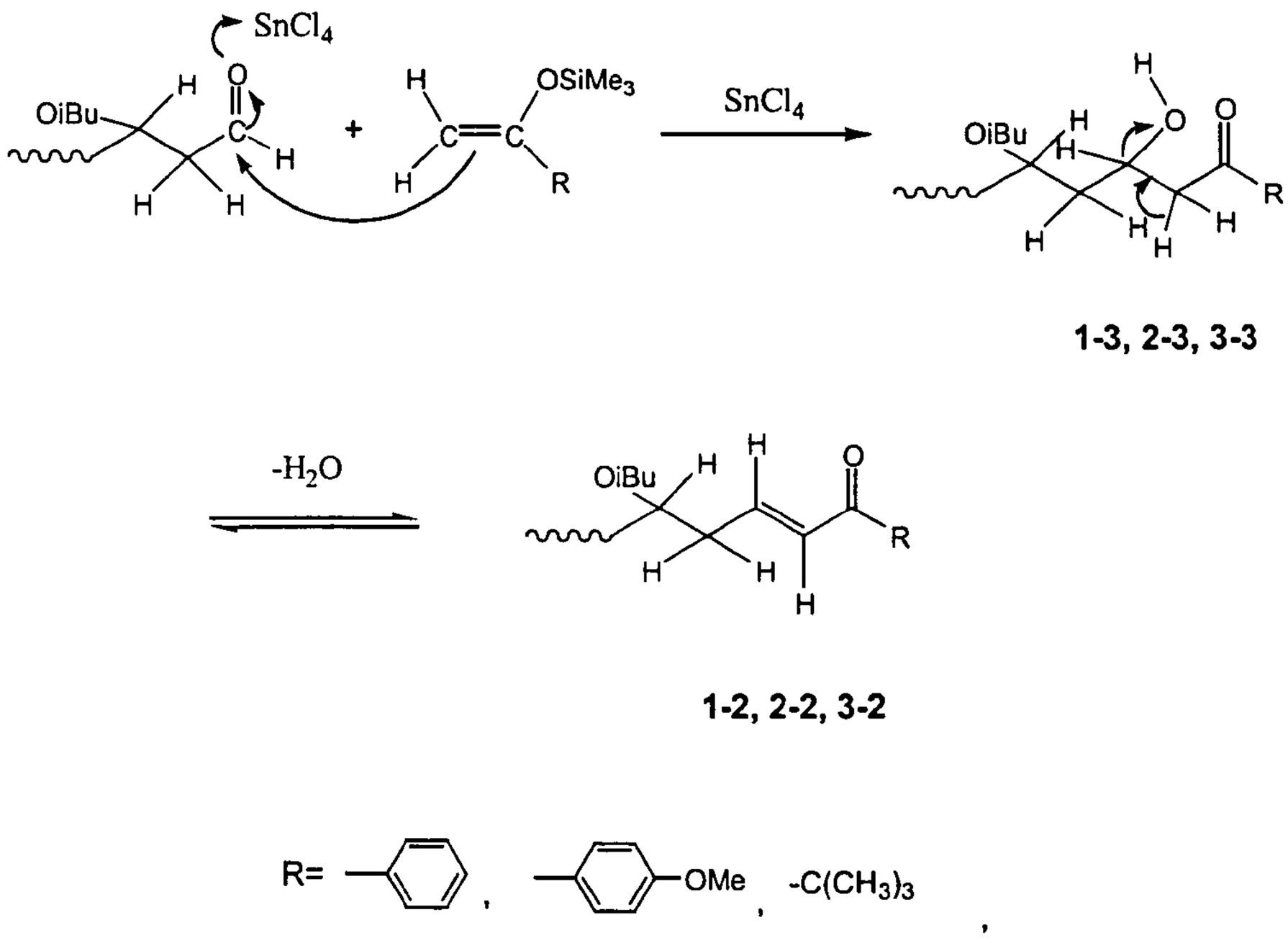
Figure 4-15: Suppression of side reactions by end-capping with silyl enol ethers under room temperature

The observation that the diisobutanol chain end **6** is present in relatively high amount among longer oligomer chains in figure 4-13 can be explained; the longer oligomer chain could have formed after the silyl enol ethers had been largely consumed.

4.3.3 The formation of various functionalised chain ends

Silyl enol ether functionalised chain ends were listed in table 4-3. It was found that silyl enol ether also reacted at other electrophilic sites apart from the carbocationic chain end.

General analysis of the cationic polymerisation of isobutyl vinyl ether revealed that the aldehyde chain end is formed, even in the quasi-living polymerisation. Indeed, the aldehyde chain end is usually observed (by NMR and MALDI-TOF MS analysis) in oligomer samples without end-capping. However it's concentration was reduced in the presence of reactive silyl enol ethers. As discussed formerly, this reduction (or disappearance) of aldehyde chain ends could be due to the higher end-capping rate when compare to the side reaction rates. An alternative means of suppression of the aldehyde chain end is capping of the aldehyde chain ends by silyl enol ether resulting in the formation of an internal alkene ketone or β-hydroxy ketone chain ends. The mechanism is shown in scheme 4-8. As introduced in chapter 1 this is a Mukaiyama-Aldol condensation reaction. In general a mixed aldol reaction between two similar ketone or aldehyde components leads to a mixture of four possible products—two symmetrical aldol products and two mixed aldol products. When one of the carbonyl components contains no α hydrogens, it cannot form an enolate ion to become a donor, so a mixed aldol reaction is likely to be successful. However, to make this reaction regioselective, enol derivatives of the ketone were applied to add to the aldehyde or ketone. A number of enolate derivatives including silyl enol ethers, have been used to ensure that coupling takes place on the desired side of an unsymmetrical ketone [Mukaiyama, 1974a].



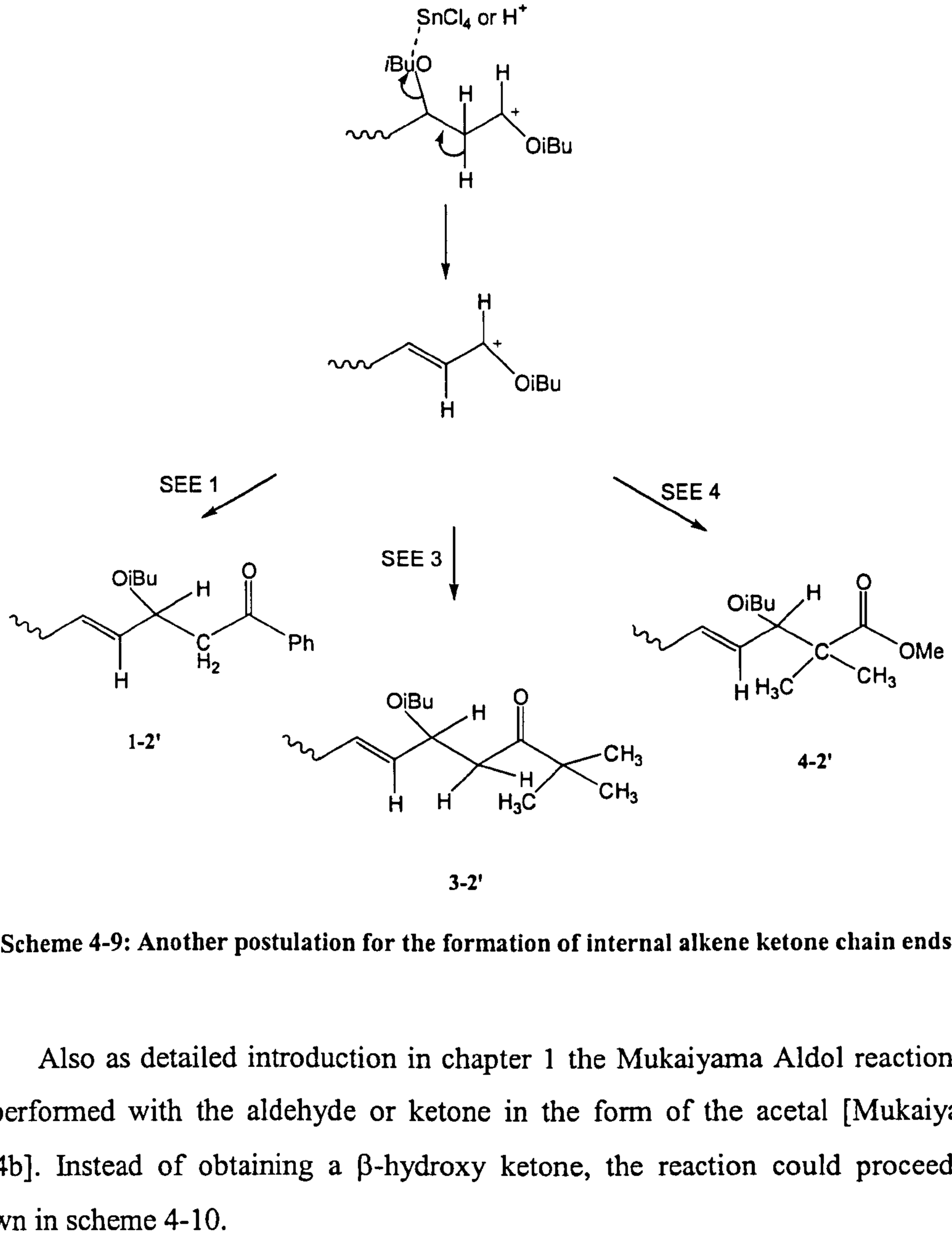
Scheme 4-8: The capping of the aldehyde chain end by silyl enol ethers

Scheme 4-8 shows the reaction between the silyl enol ether and the aldehyde chain end to form the β-hydroxy ketone. Formation of the double bond in **1-2**, **2-2** and **3-2** drives the dehydration of **1-3**, **2-3** and **3-3** to form the α,β-unsaturated ketone at the chain ends. Both the α,β-unsaturated ketone (**2-2**) and the β-hydroxy ketone (**2-3**) are often observed in MALDI-TOF mass spectra when **SEE 2** is applied in end-capping and this observation strongly supports the mechanism proposed in scheme 4-8. The dehydration step is in equilibrium and if all of the **2-2** comes from dehydration of **2-3,** it can be seen that the equilibrium favours the unsaturated ketone chain end.

1-3 is observed in the MALDI-TOF mass spectra of oligomer samples polymerised at 0° and –15°C. Unfortunately oligomer **1-2** cannot be discerned because the theoretical *m/z* value of **1-2** is the same as for oligomer 3. These observations of **SEE 1** could not be as strong evidence as **SEE 2**, still they do not provide evidence against scheme 4-8.

Although present in small amounts, the internal alkene ketone chain ends have been observed in MALDI-TOF mass spectra when the 4 reactive silyl enol ethers were applied as end-capping agents. The formation of the chain ends **1-2**, **3-2** and **4-2** (table 4-3) could also be explained by scheme 4-9; the internal alkene is formed independently while the carbocationic chain end is left living and is eventually capped

by silyl enol ethers. This scheme is also applicable when **SEE 2** is the end-capping agent.

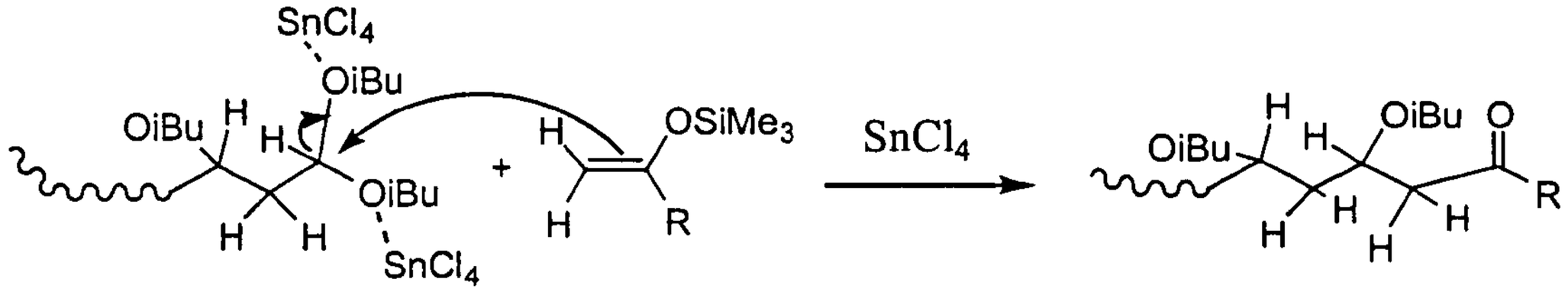


Scheme 4-9: Another postulation for the formation of internal alkene ketone chain ends

Also as detailed introduction in chapter 1 the Mukaiyama Aldol reaction can be performed with the aldehyde or ketone in the form of the acetal [Mukaiyama, 1974b]. Instead of obtaining a β-hydroxy ketone, the reaction could proceeds as shown in scheme 4-10.

The functionalised chain ends **1-1**, **2-1** and **3-1** can be formed through the end-capping of diisobutanol chain ends by silyl enol ethers. This mechanism is also applicable to **SEE 4** which largely reduces the formation of the diisobutanol chain end. The reduction in diisobutanol chain end in end-capping provides strong evidence that the diisobutanol chain ends can be suppressed in two ways. Either the higher competition rate of the end-capping reactions suppresses the formation of diisobutanol

chain end, or the silyl enol ethers cap the formed diisobutanol chain end and improves the chain end functionalities.



6	R=Ph, PhOMe, $C(CH_3)_3$	**1-1, 2-1, 3-1**

Scheme 4-10: Capping of acetal chain end by silyl enol ethers

The postulated reactions in scheme 4-9 and scheme 4-10 require further evidence apart from MALDI-TOF mass spectrum. ^{13}C NMR could help in the analysis but the very tiny amount of these chain ends made analysis difficult. It was even more difficult to identify the diisobutanol chain end using proton NMR spectroscopy.

A simple experiment could be carried out to prove the capping of acetal chain end by silyl enol ethers, i.e., mix the purified high diisobutanol chain end content OiBVE sample with Lewis acid and the reactive silyl enol ethers in DCM. After the reaction, the reduction in concentration of the diisobutanol chain end and the presence of chain end functionalities in the recovered oligomer samples provide confirmation of the reaction outlined in scheme 4-10. The same method can also prove the capping of aldehyde chain end by silyl enol ethers.

4.3.4 End-capping of silyl enol ether **1** and **2**

In our research **SEE 1** and **SEE 2** generally showed high reactivity in end-capping. The experimental results indicate that **SEE 2** has a higher reactivity than **SEE 1**. This was not difficult to understand. The *para*-methoxy substitute activated the aromatic ring and thus activated the silyl enol ether. Table 4-4 compares the OiBVEs obtained from polymerisations without end-capping and with the end-capping by **SEE 1** and **2** prepared under various reaction temperatures. Polymerisation conditions, SEC analysis results as well as the chain end functionality data from the respective ^1H NMR analysis are listed in the table.

Table 4-4: Comparison of OiBVE data from parallel polymerisations with and without end-capping

Monomer	Additive	SEE[α)]	Temperature[β)] °C	M:I:SEE[γ)]	M_n	PD	Fn[δ)] %	Conversion[ε)] %
iBVE	None	None	21	10:1:0	870	2.24	-	58.1
		1	21	10:1:1	760	2.61	58.1	74.2
		2	21	10:1:1	740	2.70	52.0	54.7
iBVE	None	None	0	10:1:0	770	1.74	-	59.4
		1	0	10:1:1	760	2.67	46.6	88.0
		2	0	10:1:1	750	2.78	55.7	71.4
iBVE	None	None	-15	10:1:0	1010	1.89	-	68.4
		1	-15	10:1:1	960	2.45	69.7	75.2
		2	-15	10:1:1	750	2.33	34.0	86.5
iBVE	*n*-Bu_4NCl	None	-15	10:1:0	760	1.62	-	81.8
		1	-15	10:1:1	900	2.08	46.0	84.6
		2	-15	10:1:1	650	8.09	95.9	90.6
iBVE	None	None	-78	10:1:0	940	1.56	-	100
		1	-78	10:1:1	590	2.07	85.8	81.5
		2	-78	10:1:1	850	2.85	64.6	100

Polymerisation time is 60 minutes. Initial [iBVE]=0.38 mol L^{-1}

α): Silyl enol ether being applied in polymerisation

β): Polymerisation temperature

γ): Initial initiation ratio is [iBVE]:[IBVE-HCl]:[SEE]:[$SnCl_4$]:[*n*-Bu_4NCl]=10:1:1:0.5:0.75

δ): Chain end functionalities are obtained from integration of proton NMR of the applicable samples

ε): Monomer conversions are obtained by comparing the oligomer yield and initial monomer amount

Both the end-capping of **SEE 1** and **SEE 2** lead to moderate PD of the oligomer samples. **SEE 2** functionalised OiBVEs have broader PD than the oligomer samples end-capped by **SEE 1**. Also, **SEE 2** capped oligomers had a lower molecular weight than the OiBVEs from the parallel polymerisations without end-capping. At -15°C in the presence of added nucleophile, **SEE 1** gave oligomers with higher chain

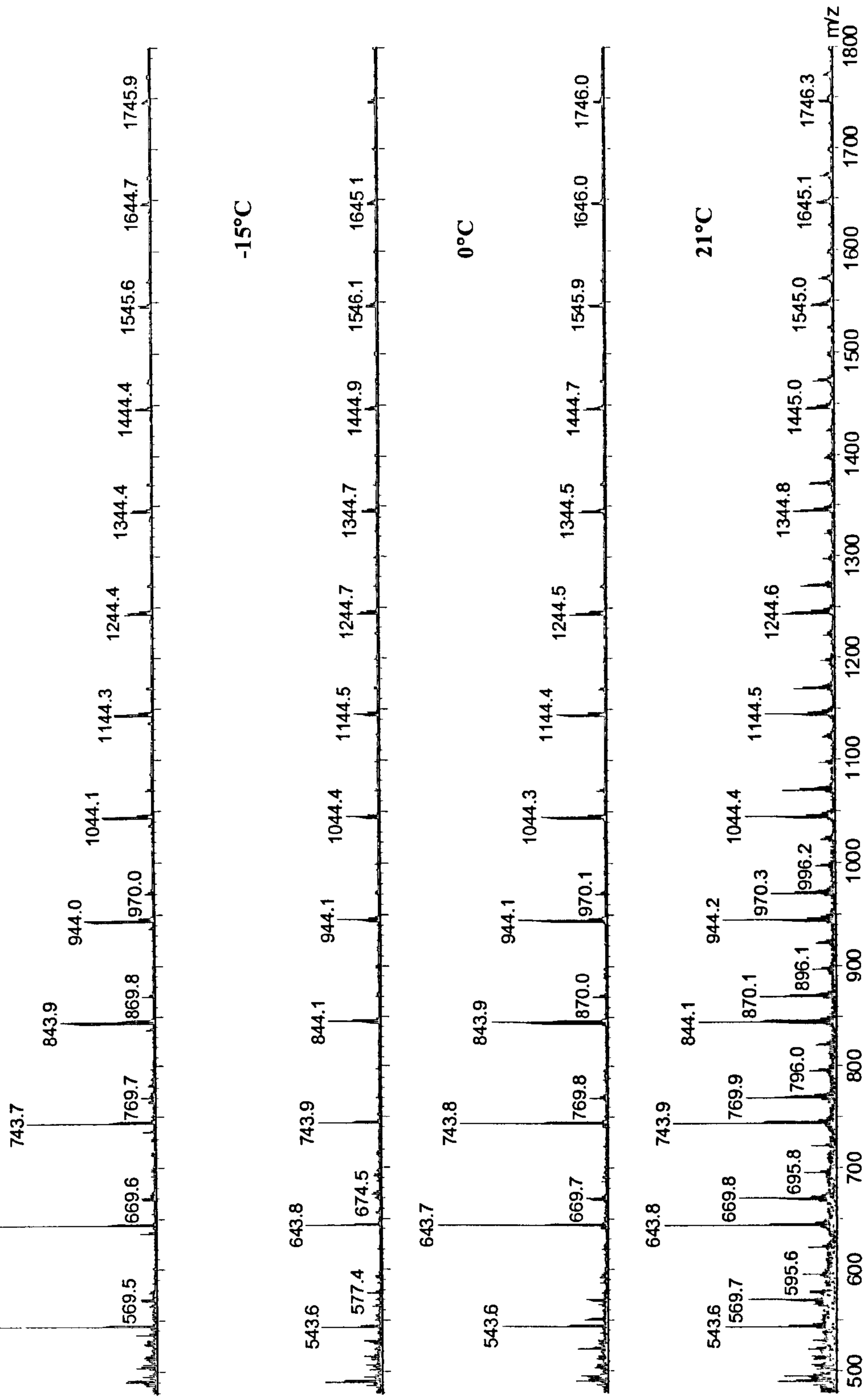


Figure 4-16: MALDI-TOF mass spectra of OiBVEs end-capped by SEE 1

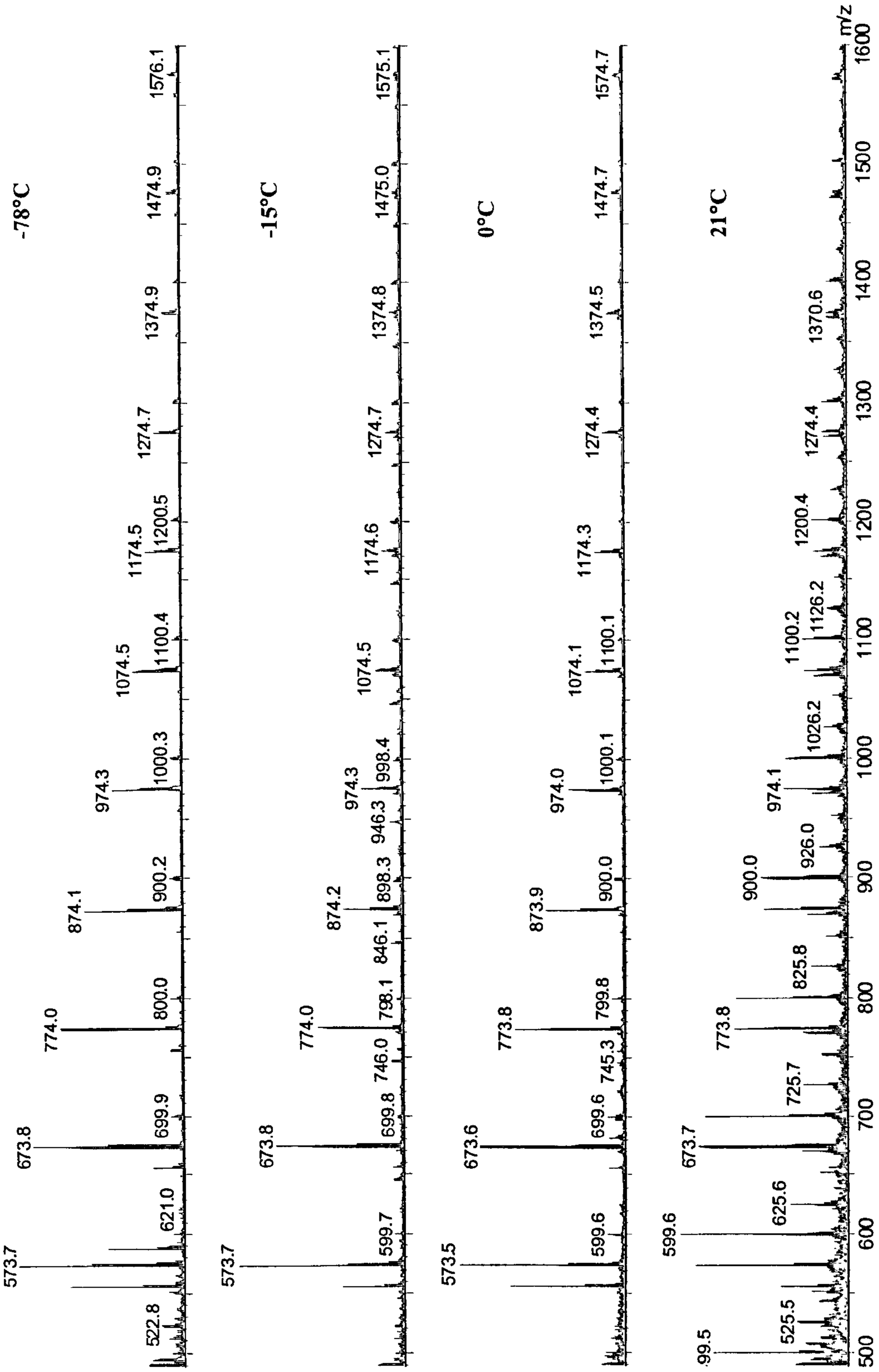


Figure 4-17: MALDI-TOF mass spectra of OiBVEs end-capped by SEE 2

length than oligomers from the parallel polymerisation without end-capping. In accordance with the higher M_n observed in the end-capping, the chain end functionality obtained was lower than usual. The observation indicated the effect of nucleophiles on end-capping and this will be discussed in detail separately. It can be seen from the table that low temperature generally helped increase chain end functionality.

Figure 4-16 and figure 4-17 are MALDI-TOF mass spectra of the same oligomer samples end-capped by **SEE 1** and **SEE 2** listed in table 4-4. It can be seen from most of the spectra that the oligomer chain end functionalities are higher than the data obtained from ^{1}H NMR, which come from comparison of the integration values on both α-end and ω-end protons. ^{1}H NMR measurement would be more accurate if an accurate integration value could be obtained. Sometimes when overlaps happen it is impossible to obtain chain end functionality data via NMR, and MALDI-TOF MS can thus provide very helpful information on chain end functionality. This will be discussed in detail in chapter 5.

Figure 4-18 gives the combined expanded MALDI-TOF mass spectra of OiBVE end-capped by **SEE 1** containing two repeat units so that the details of the oligomer are shown. Figure 4-18 shows that at room temperature when **SEE 1** is applied the chain end was partially functionalised. The 100n+70 Daltons oligomer series appeared to have the second intensity in the spectrum. It is postulated that the peak is due to either primary hydroxy chain end **3** or the internal alkene ketone chain end **1-2**. At 0°C apart from the large amount of **SEE 1** functionalised chain end, the 100n+70 signal also appears, as well as the postulated Mukaiyama-Aldol product of **1-3**, with the approximate ion mass of 100n+88 Daltons. At -15°C the 100n+70, 100n+98 appear indicating the presence of small amount of diisobutanol chain end and the possible hydroxy chain end, or internal alkene ketone chain end. At -78°C, again a small amount of 100n+70 signal as well as the unknown 100n+36 signal are observed.

Figure 4-19 shows the combined expanded MALDI-TOF mass spectra of OiBVE samples end-capped by **SEE 2,** containing details of the chain end functionalisation and side reactions during the polymerisations. In general compared with the oligomer samples end-capped by **SEE 1**, the oligomer samples end-capped by **SEE 2** have a higher amount of side reaction chain ends.

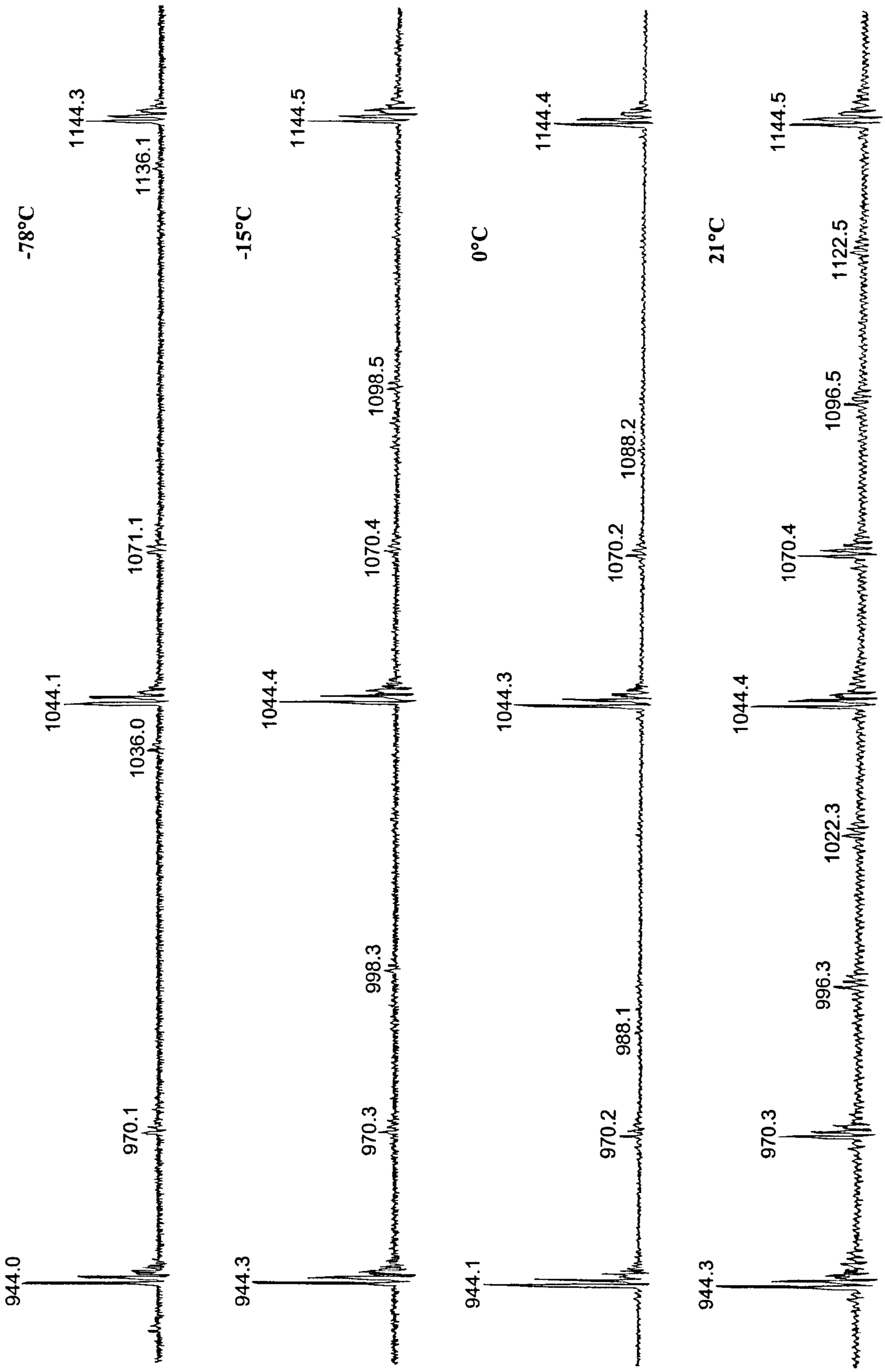


Figure 4-18: Expanded MALDI-TOF mass spectra of OiBVE end-capped by SEE 1 at different temperatures

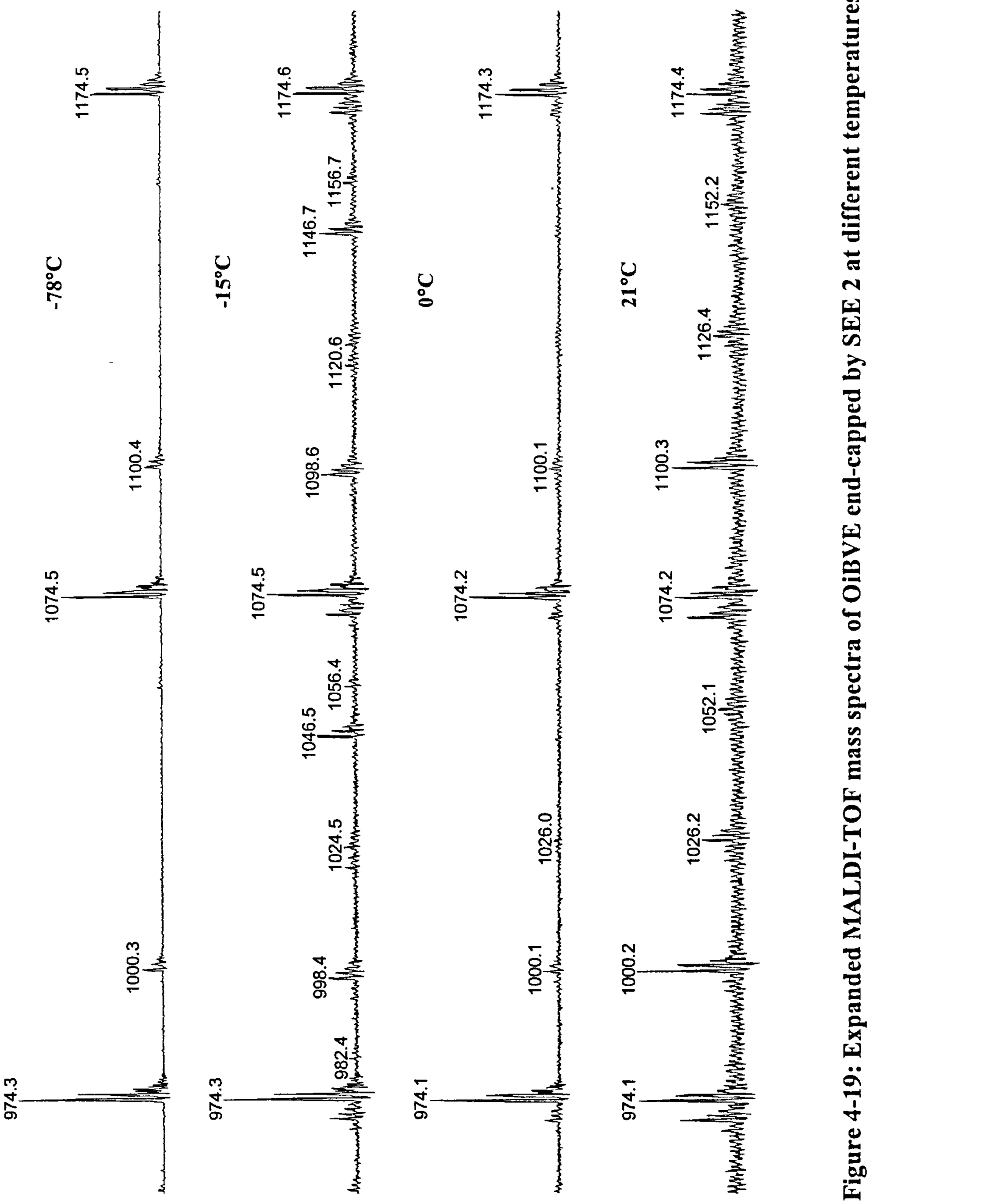


Figure 4-19: Expanded MALDI-TOF mass spectra of OiBVE end-capped by SEE 2 at different temperatures

At room temperature (21°C) the two major oligomer ion series present were found to be the **SEE 2** functionalised **1-1** and **1-2**, indicating higher amount of internal alkene ketone chain end despite the fact that the alkene chain end from chain transfer is not observed. This indicates that either the side reaction of β-proton elimination, which has a higher reaction rate at this temperature, is suppressed by other side reactions, or this internal alkene ketone chain end **1-2** come from the dehydration of the aldol product (shown in Scheme 4-8). The diisobutanol chain end is not observed although a higher amount of internal alkene ketone chain results in a large amount of isobutanol being released during the polymerisation (and present in the system). This observation supports the idea that the suppression of the diisobutanol chain end can be achieved by either higher end-capping reaction rate compared to isobutanol capping or the capping of diisobutanol chain ends by **SEE 2**. At this relatively high polymerisation temperature, the unknown oligomer ion masses of 100n+26 and 100n+52 are also observed as well as the 100n+70 signal.

The aldol product **1-3** (with the *m/z* value of 100n+88 Daltons) is only formed in a tiny amount at the low temperature of -78°C, and it disappears at all other temperatures. Either enhanced dehydration of the aldol product or a reduction in the amount of aldol reaction can lead to this result. Low temperature helped to suppress the side reactions and the expanded spectrum is shown to be a cleaner **SEE 2** functionalised oligomer with only **2-1** and **2-2** present in the low molecular weight range.

From table 4-4, it can be seen that oligomer samples end-capped by **SEE 2** have lower M_n than their parallel polymerisation products without end-capping and they also exhibit broader PD. SEC of the OiBVE samples end capped by **SEE 2** showed multimodal distributions. The MALDI-TOF spectra of these samples showed bimodal distributions. The lower the polymerisation temperature, the more apparent the bimodal distribution of the oligomer. Multimodal molecular weight distributions have been observed in cationic polymerisations. For example, trimodal molecular weight distributions were observed in the polymerisation of *p*-methoxystyrene [Kunitake, 1975] and this was explained as three independently growing species with different reactivities.

In the current polymerisation system control polymerisations in the absence of silyl enol ether have mono-modal molecular weight distributions. So that the

multimodal molecular weight distributions obtained are probably due to end-capping by silyl enol ether and need to be explained.

Figure 4-20 shows the MALDI-TOF mass spectrum of OiBVE end capped by **SEE 2** at –78°C. In figure 4-20 the oligomer series end-capped by **SEE 2** appears to have higher intensity in the low molecular weight range, and another oligomer series with the methoxy chain end has high intensity in the higher molecular weight range. Both the SEC and MALDI-TOF results can be explained by the higher reactivity of silyl enol ether 2. Low temperature suppresses many side reactions. If the oligomer chain end is not capped by **SEE 2**, it can be largely left living. Due to the high reactivity of **SEE 2** in end-capping it is consumed quickly and highly functionalised short oligomer chains are formed. The highly functionalised short oligomer chain can be observed in both figure 4-20 and the MALDI-TOF spectrum of oligomer sample polymerised at -78°C (figure 4-17). After **SEE 2** was largely consumed, the end-capping rate tended to be low but the living chain continued to propagate to form longer polymer chains, capped by isobutanol or eventually quenched by methanol. Methoxy chain end (100n+58), diisobutanol chain end (100n+0) as well as **SEE 2** functionalised chain end (100n+76) were observed in the higher molecular weight range in the expanded spectrum in figure 4-20.

Comparison of the chain end functionality data from table 4-4 reveals that although **SEE 2** is supposed to have a higher reactivity in end-capping, it does not necessarily produce a higher chain end functionality than **SEE 1** without the presence of a deactivator.

MALDI-TOF mass spectra (figures 4-16, 4-17, 4-18 and 4-19) also support the conclusion that high end-capping reactivity does not always lead to high chain end functionality. The reason could be that **SEE 2** is too reactive in end-capping. A suitable end-capping rate compared with chain propagation rate is required in end-capping for maximum reduction of side reactions and a controlled cationic polymerisation.

From table 4-4, it can also be seen that oligomer samples end-capped by **SEE 2** have the highest chain end functionality at -15°C and in the presence of added nucleophile, while **SEE 1** has the highest chain end functionality at lowest temperature.

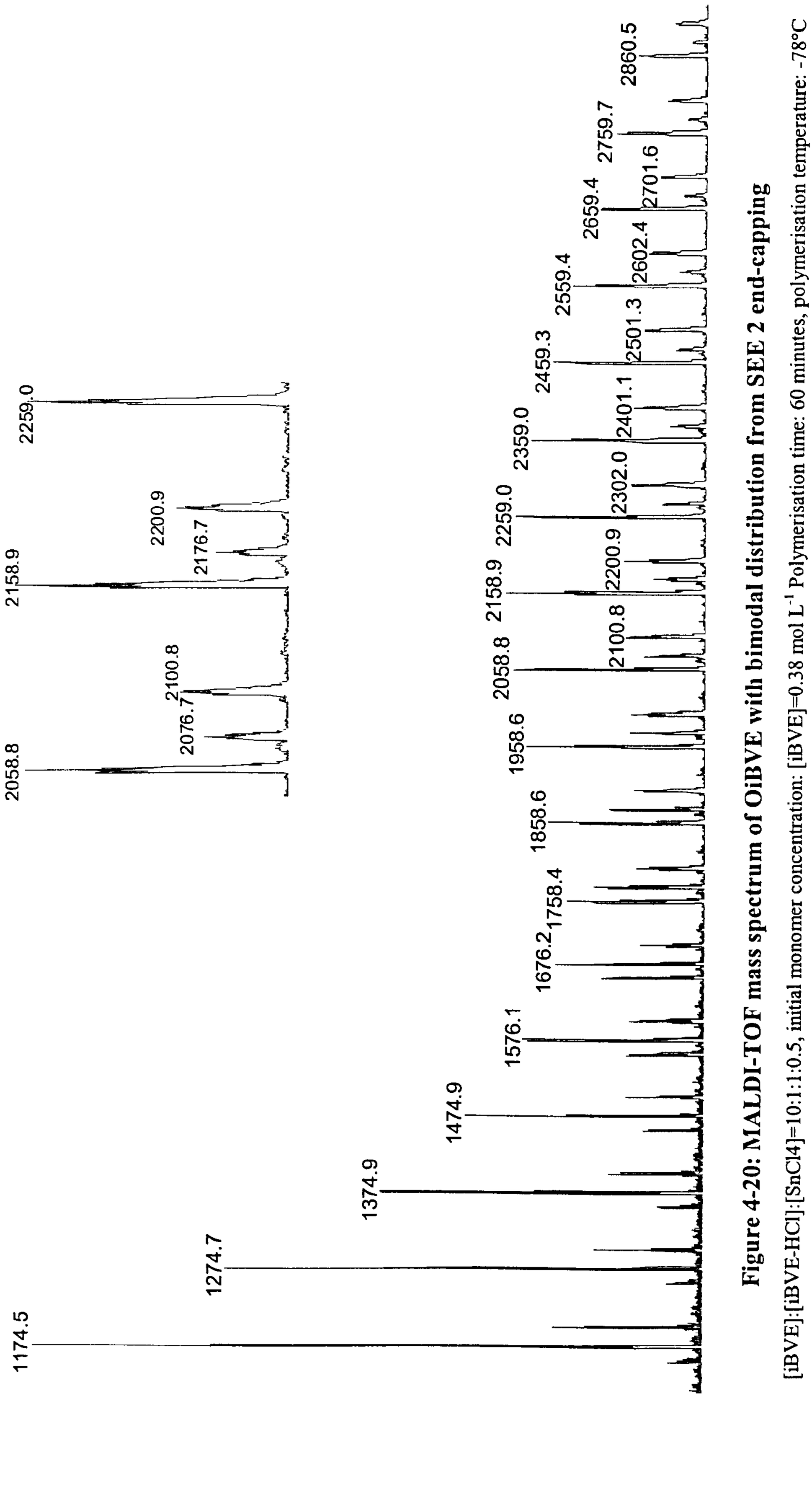


Figure 4-20: MALDI-TOF mass spectrum of OiBVE with bimodal distribution from SEE 2 end-capping

[iBVE]:[iBVE-HCl]:[$SnCl_4$]=10:1:1:0.5, initial monomer concentration: [iBVE]=0.38 mol L^{-1} Polymerisation time: 60 minutes, polymerisation temperature: -78°C

4.3.5 End-capping with silyl enol ether **3**

As well as producing the chain end functionality and suppressing side reactions, end-capping could also help to produce a well-defined cationic polymerisation. Table 4-5 shows the polymerisation data with end-capping by **SEE 3**. SEC overlays of OiBVEs end capped by **SEE 3** have monomodal distributions. Combined with the data from table 4-4, the **SEE 3** capped oligomers have narrower polydispersity than the identical oligomer samples without end-capping at all polymerisation temperatures. This may be because the end-capping rate suppresses side reactions and causes the PD to be narrower. It is also possible that the silyl enol ether nucleophile acts as an additive in the cationic system to affect the chain initiation, chain propagation and reduce chain transfer, thus giving the narrow PD.

Table 4-5: End-capping by silyl enol ether 3 – OiBVE data

Monomer	Lewis acid	Additive	SEE[α)]	Temp[β)] °C	M:I:SEE[γ)]	M_n	PD	Fn[δ)] %	Conversion[ε)] %
iBVE	$SnCl_4$	None	**SEE 3**	21	10:1:1	940	2.11	N/A	79.4
		None		0		820	1.89	N/A	86.2
		None		-15		850	1.72	N/A	91.4
		n-Bu_4NCl		-15		910	1.51	N/A	94.0
		None		-78		1380	1.31	N/A	100

Polymerisation time is 60 minutes. Initial monomer concentration: [iBVE]=0.38 mol L^{-1}

α): Silyl enol ether being applied in polymerisation

β): Polymerisation temperature

γ): Initial initiation ratio is [iBVE]:[iBVE-HCl]:[SEE]:[$SnCl_4$]:[*n*-Bu_4NCl]=10:1:1:0.5:0.75

δ): Quantitative proton NMR analysis is not applicable due to the overlapping of α-end proton resonances and ω-end proton resonances.

ε): Monomer conversions are obtained by comparing the oligomer yield and initial monomer amount

Another observation in table 4-5 is that oligomer samples end-capped by **SEE 3** have higher M_n than their parallel polymerisation samples without end-capping. This could be evidence of the relatively lower reactivity of **SEE 3** than **SEE 1** and **SEE 2** in end-capping.

However, this observation is in conflict with the observation when ytterbium triflate was applied as co-initiator. When ytterbium triflate was used, oligomers end-

capped by **SEE 3** always have a lower molecular weight than the parallel oligomer samples without end-capping. This conflict cannot be explained.

Figure 4-21 shows the C-H correlation NMR of OiBVE sample end-capped by **SEE 3**. From the spectrum it can be seen that the overlapped proton resonances of α-end methyl and ω-end methyl groups at 1.1 ppm are separated on 2-D NMR. The upper blue circle indicates the resonance of the α-end methyl group that correlates to ^{13}C resonance at 18 ppm; the lower red circle indicates the resonances of ω-end methyl groups, which correlates to the ^{13}C resonance at 27 ppm. Polymer chain end functionalities cannot be obtained from NMR integration because of this overlap of chain end resonances.

Figure 4-22 and figure 4-23 give the full and expanded MALDI-TOF mass spectra of the **SEE 3** functionalised oligo (isobutyl vinyl ether)s. In these spectra the prominent end-functionalised oligomer chain end, diisobutanol and other side reaction chain ends are observed. Side reactions are reduced in the presence of **SEE 3** but they still can be observed at all polymerisation temperatures. Apparently the low temperature helped to reduce the side reactions. A higher amount of internal alkene ketone chain end **3-2** (with the oligomer ion mass of 100n+50) is observed at higher polymerisation temperature. Two main chain ends resulting from side reactions were assigned as diisobutanol chain end (100n+98) and the postulated primary alcohol chain end (100n+70).

The observations of the prominent functionalised chain end and the suppressed side reactions in the MALDI-TOF mass spectra plus narrower PD from SEC analysis indicate that end-capping with **SEE 3** occurs at a suitable rate, which is higher than the majority of the side reaction rates but lower than the chain propagation rate. Therefore high chain end functionality is obtained but the molecular weight distribution has not been broadened.

4.3.6 End-capping with **SEE 4**

SEE 4 was applied because, after the end-capping, it produces ester functional groups at the oligomer chain ends. This silyl enol ether was developed by Du Pont in 1983 [Cowie, 1991] as an initiator in group transfer polymerisation

Table 4-6 shows the polymerisation data with the end-capping by **SEE 4**.

Table 4-6: End-capping with SEE 4—OiBVE data

Monomer	Lewis acid	Additive	SEE[α)]	Temp[β)] °C	M:I:SEE[γ)]	M_n	PD	Fn[δ)] %	Conversion[ε)] %
iBVE	$SnCl_4$	None	SEE 4	21	10:1:1	750	2.54	N/A	58.6
		None		0		850	2.26	N/A	76.3
		None		-15		1030	2.12	N/A	78.1
		n-Bu_4NCl		-15		930	2.37	N/A	57.6
		None		-78		1210	2.20	N/A	100

Polymerisation time is 60 minutes. Initial monomer concentration: [iBVE]=0.38 mol L^{-1}

α): Silyl enol ether being applied in polymerisation

β): Polymerisation temperature

γ): Initial initiation ratio is [iBVE]:[iBVE-HCl]:[SEE]:[$SnCl_4$]:[*n*-Bu_4NCl]=10:1:1:0.5:0.75

δ): Quantitative proton NMR analysis is not applicable due to the overlapping of α-end proton resonances and ω-end proton resonances.

ε): Monomer conversions are obtained by comparing the oligomer yield and initial monomer amount

The polymerisation results with end-capping by **SEE 4** are different compared with **SEE 1**, **SEE 2** and **SEE 3**. **SEE 1** and **SEE 2** are highly reactive and lead to lower M_n than the control polymerisations without end-capping, their MALDI-TOF spectra also show highly functionalised oligomer chains. **SEE 3**, was found to be reasonably reactive and gave fairly high chain end functionality and narrower PD. The **SEE 4**-capped oligomer has broader molecular weight distribution as well as relatively low chain end functionality. Polymerisations in the presence of **SEE 4** gave higher M_n than control polymerisation, especially at low temperature of -78°C. Chain end functionality is low at room temperature. Figure 4-24 shows the MALDI-TOF mass spectra of oligomers end-capped by **SEE 4** under different temperatures. Figure 4-25 shows the expanded spectra.

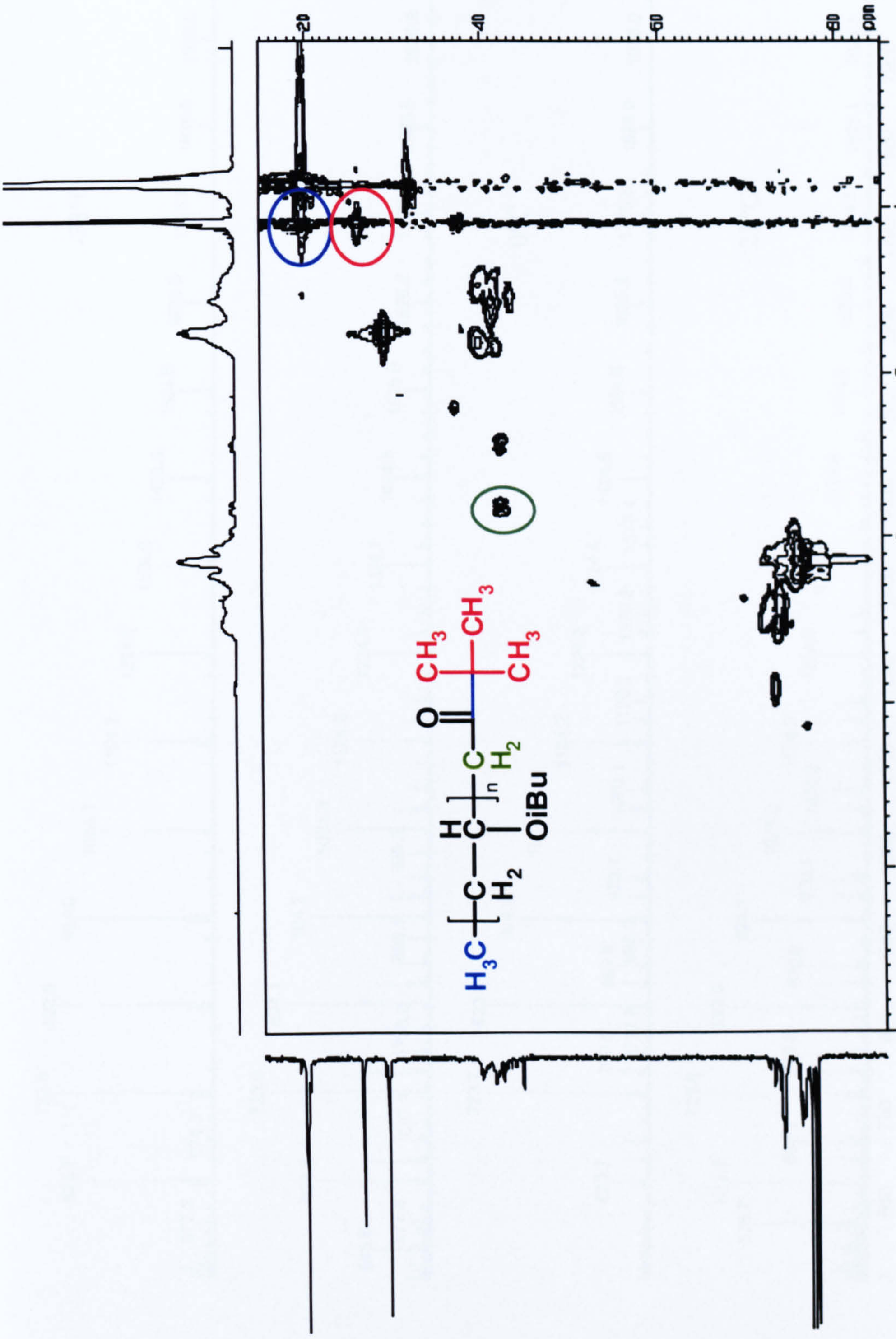


Figure 4-21: C-H correlation NMR of OiBVE end-capped by SEE 3

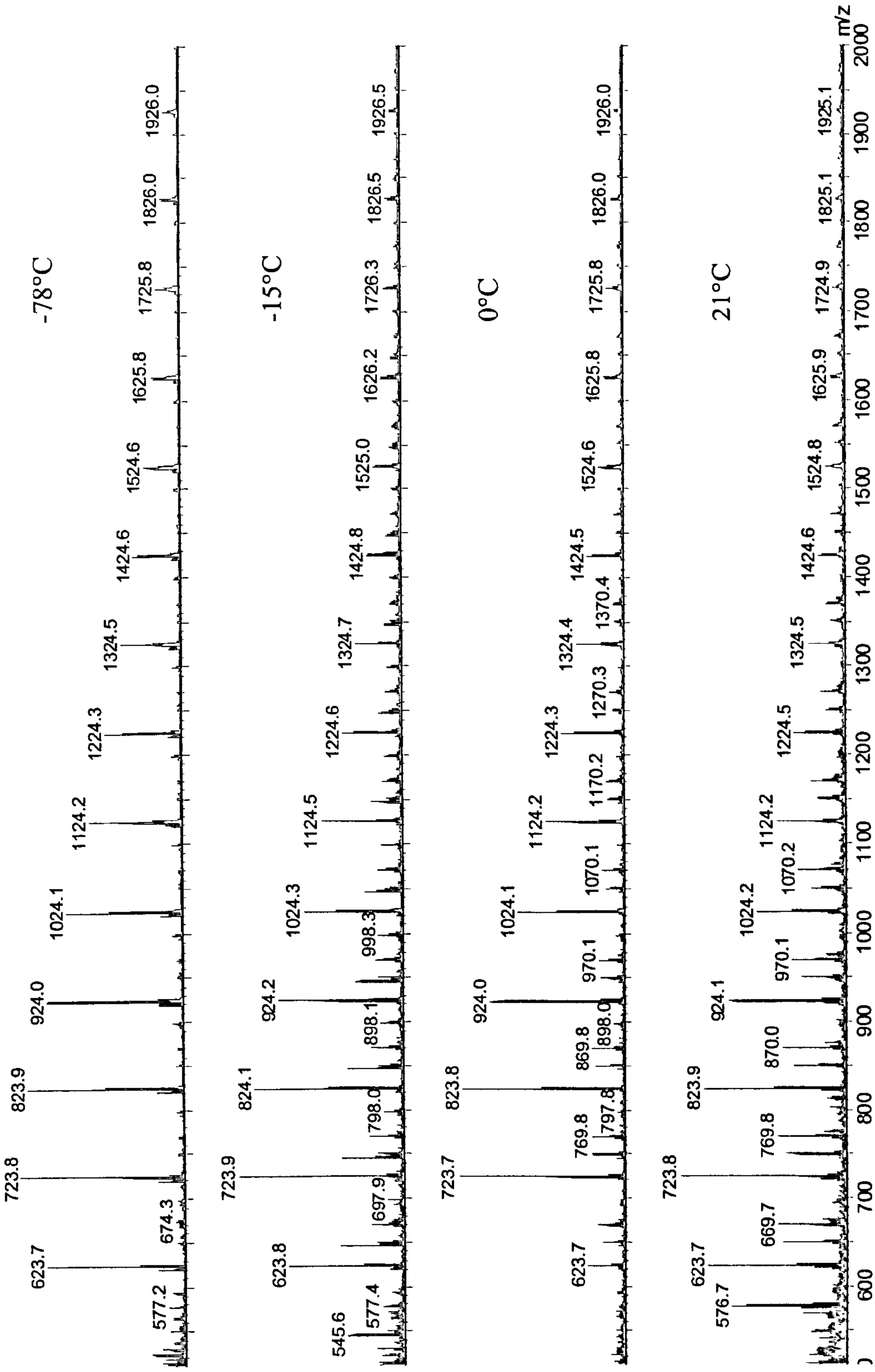


Figure 4-22: MALDI-TOF mass spectra of OiBVE end-capped by SEE 3 at different temperatures

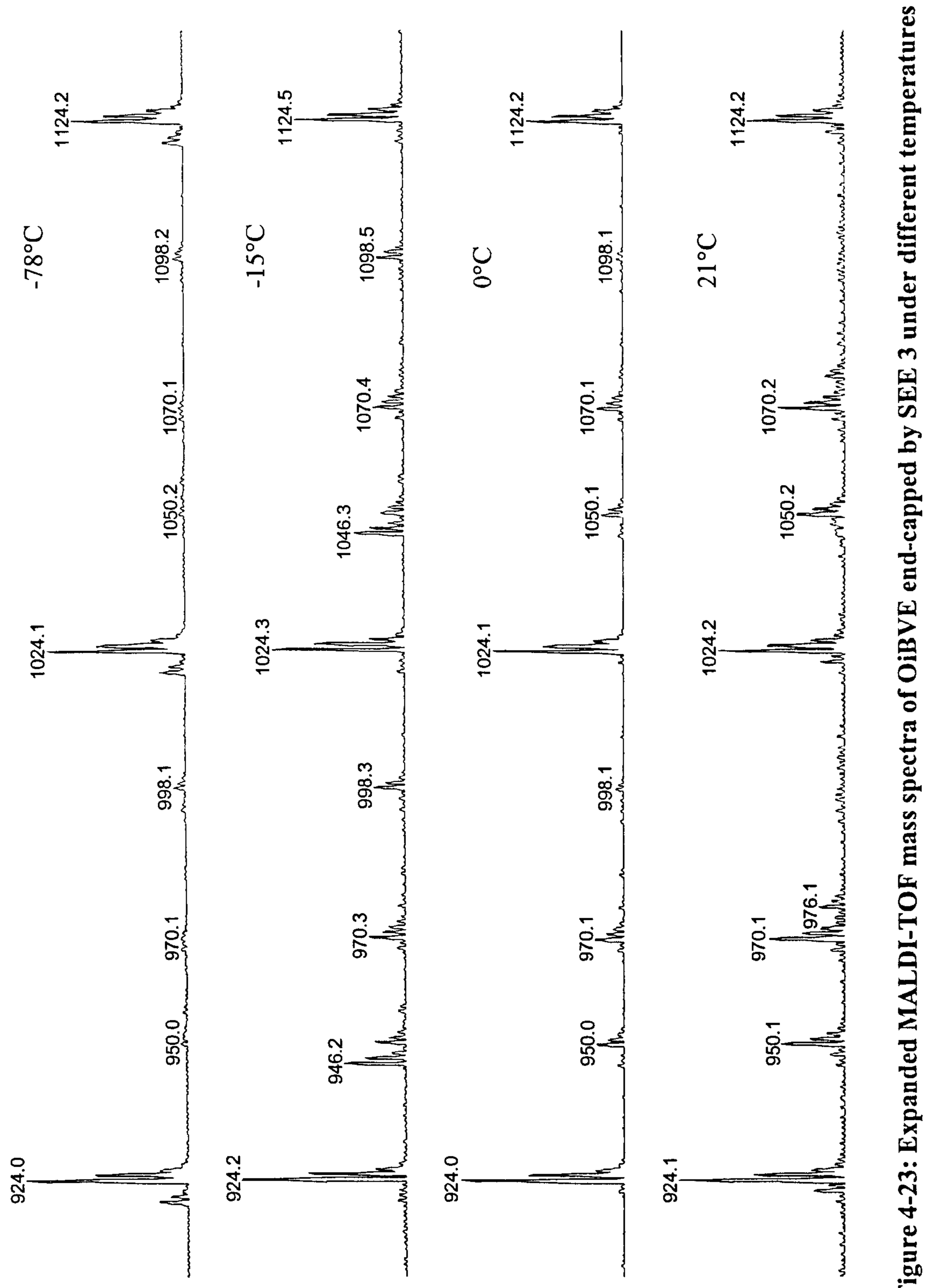


Figure 4-23: Expanded MALDI-TOF mass spectra of OiBVE end-capped by SEE 3 under different temperatures

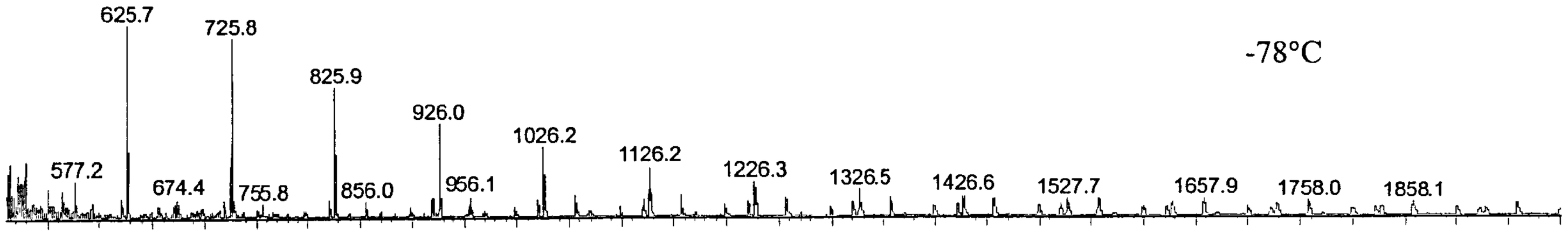


Figure 4-24: MALDI-TOF mass spectra of OiBVE end-capped by SEE 4 under different temperatures

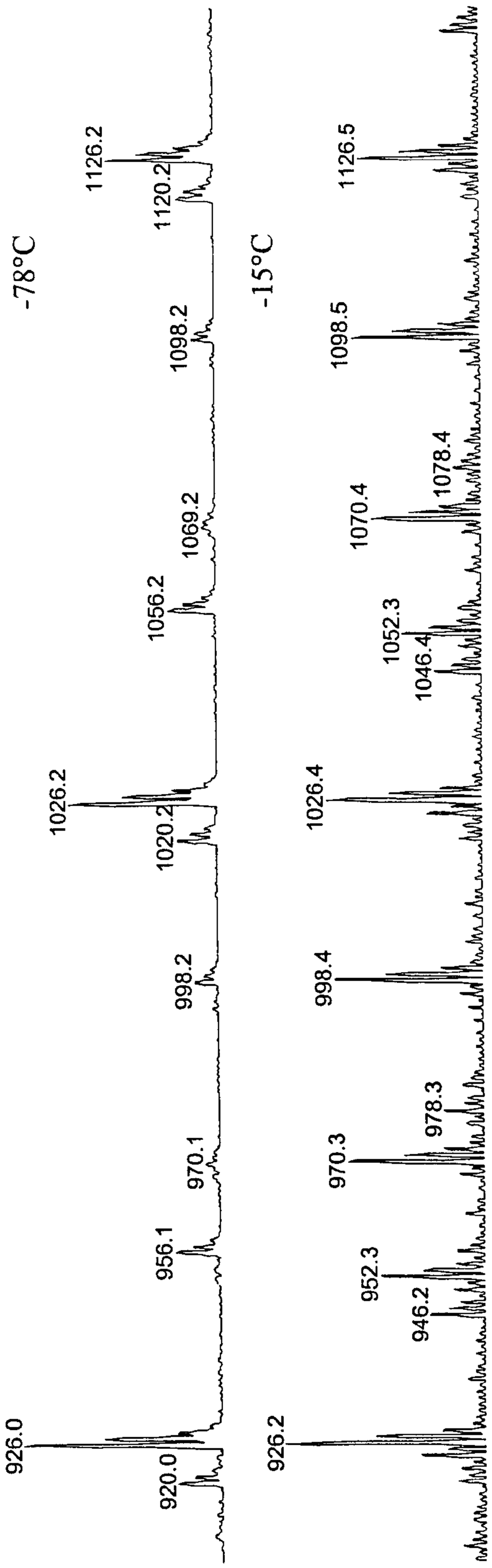


Figure 4-25: Expanded MALDI mass spectra of OiBVE samples end-capped by SEE 4 under different temperatures

From the MALDI result it was found that end-capping with **SEE 4** at the low temperature of -78°C gave high chain end functionality (with the oligomer ion mass of 100n+26). A large amount of internal alkene ketone chain end **4-2** (with the oligomer ion mass of 100n+52) was observed at -15°C, 0°C and 21°C, as well as the alkene (100n+24), diisobutanol (100n+98) and the possible primary alcohol chain end (100n+70). **SEE 4** appears to be less reactive in end-capping at raised temperatures.

4.3.7 The effect of added salt on end-capping by silyl enol ethers

To obtain a living cationic system, salts as well as nucleophiles are often added to the polymerisation. Disagreements exist on the effect of these nucleophiles.

According to Aoshima and Higashimura [Higashimura, 1989], the presence of electron donors stabilises carbocations, decreases the reactivity of propagating species, and prevents chain transfer, termination and other side reactions, so that living polymerisation can occur. Kennedy suggests that the electron donors stabilise the carbocationic chain end or change its property, reduce the reactivity of the chain end, so that the side reactions are reduced [Kennedy, 1991; Si, 1994]. Faust and Storey proposed that the electron donor is a proton trap during the polymerisation and that they reduce the chain transfer to the monomer. Sigawalt and Matyjaszewski have the opinion that these nucleophiles improve or enhance the initiation to give a higher relative initiation rate than chain propagation rate. This is fast initiation and it can be assumed that all chain propagations start at the same time. When there is enough carbocationic chain end compared with the monomer, chain transfer can be ignored and this produces a living polymerisation [Matyjaszewski, 1996; Xiang, 1992].

Addition of nucleophiles in the $Yb(OTf)_3$ initiation system led to a slower and more controlled polymerisation and this is in accordance with other reports in the literature. Addition of *n*-Bu_4NCl to the $SnCl_4$ initiation system at low temperature of -78° leads to a controlled polymerisation as shown in figure 4-2.

From table 4-4 it can be seen that **SEE 1** gives lower M_n and Fn in the presence of *n*-Bu_4NCl. **SEE 2** is a more active end capping agent and therefore shows the highest chain end functionality in the presence of *n*-Bu_4NCl. Figure 4-26 compared the MALDI-TOF mass spectra of OiBVE polymerised at -15°C with and without the presence of *n*-Bu_4NCl. In the presence of *n*-Bu_4NCl, chain end

functionality is largely improved and side reactions are significantly reduced. At the same time, table 4-4 shows that the PD of the oligomer is largely increased.

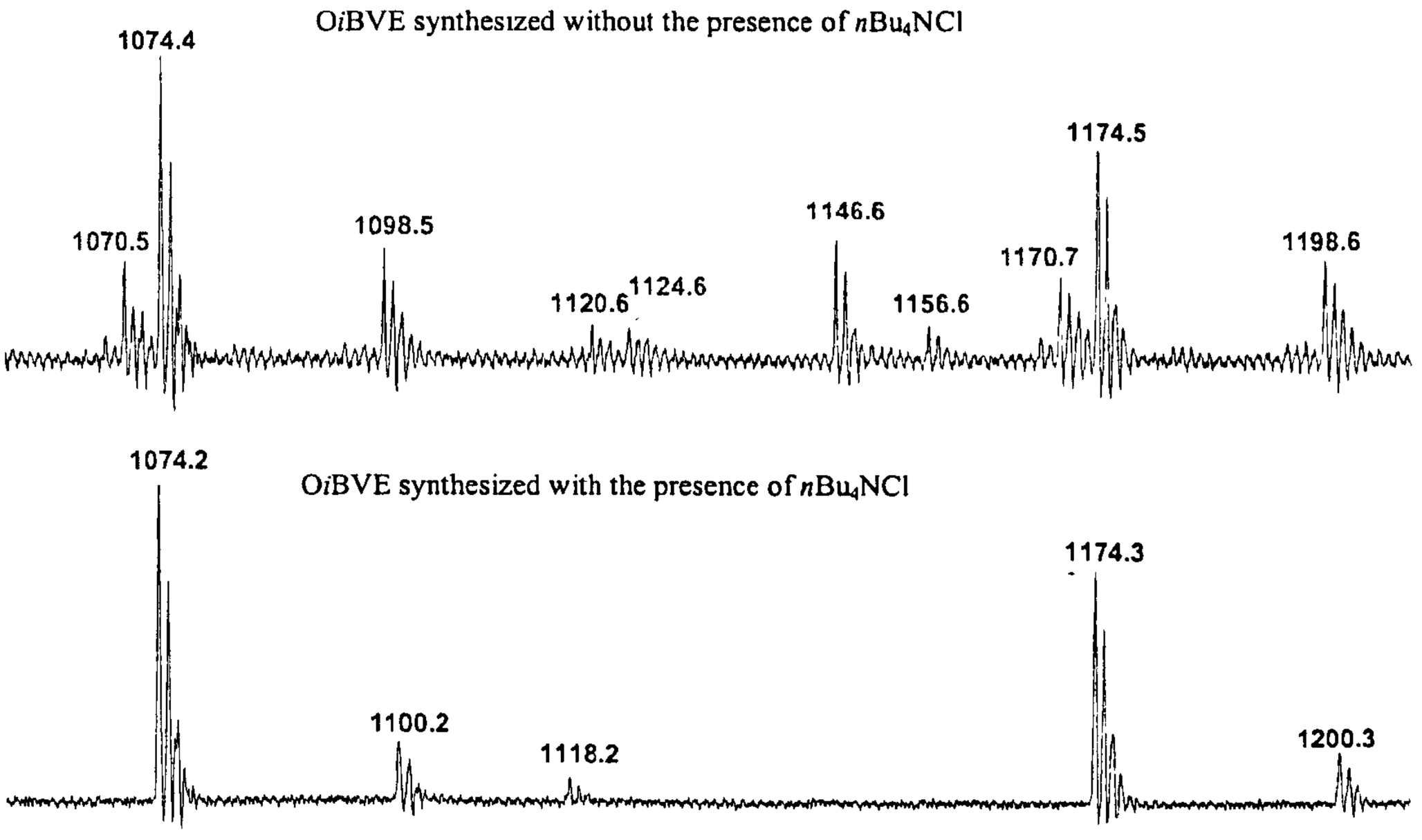


Figure 4-26: End-capping by SEE 2 in the presence and absence of added nucleophile (-15°C)

Upper polymerisation without added salt: initial [iBVE]=0.38 mol L^{-1} , [iBVE]:[iBVE-HCl]: [SEE 2]:[$SnCl_4$]=10: 1: 1: 0.5, polymerisation temperature: -15°C, polymerisation time: 60 minutes, M_n=751, PD=2.33, Fn=34.0%

Lower polymerisation with added salt: initial [iBVE]=0.38 mol L^{-1} , [iBVE]:[iBVE-HCl]: [SEE 2]:[$SnCl_4$]: [*n*-Bu_4NCl] =10: 1: 1: 0.5: 0.75, polymerisation temperature: -15°C, polymerisation time: 60 minutes, M_n=650, PD=8.09, Fn=95.9%

4.3.8 Other effects of silyl enol ethers observed

SEE 5 was found to be inactive in end-capping but it does however seem to exert an influence on cationic polymerisation. The presence of **SEE 5** generally gives a broader PD than the parallel polymerisation without end-capping, except at -78°C. As shown in table 4-7 at this low temperature the resultant OiBVE sample has narrower PD and very long polymer chains as well as low monomer conversion. The MALDI-TOF mass spectrum of the sample shows reduced side reactions and better oligomer ion distribution compared to the parallel sample. The dominant chain end is methoxy chain end formed at quenching. The limited chain ends from side reaction observed include the diisobutanol, aldehyde, and alkene chain ends.

Table 4-7: The presence of SEE 5 in the polymerisation of isobutyl vinyl ether at low temperature

Monomer	Lewis acid	Additive	SEE	Temp °C	M:I:SEE	Time min	M_n	PD	Fn %	Conversion %
iBVE	$SnCl_4$	None	5	-78	10:1:0	60	935	1.56	-	100
iBVE	$SnCl_4$	None	5	-78	10:1:1	60	2355	1.31	0	41.9

Initial monomer concentration: [iBVE]=0.38 mol L^{-1}

This result indicates **SEE 5** has an effect on the cationic polymerisation of iBVE at -78°C. Reduced initiation, reduced chain transfer and other side reactions, reduced chain initiation could lead to the high M_n, lower PD and lower monomer conversion. This observation is similar to that with the polymerisation of MVE in the presence of **SEE 4** at -78°C. In both polymerisations, M_n are abnormally high, with lower PD than the parallel sample without end-capping. Functionalised chain ends were not found.

There is something in common between these two silyl enol ethers; they both have methoxy groups attached to the sp^2 hybridized carbon. The overlapping of a *p* orbital on the oxygen with a *p* orbital on the alkene carbon results in donation of electrons through π bonds. π Electrons flow from the substituent to the alkene and enhance the electron density on the double bond of silyl enol ethers. It is reported that proton trapper could help to maintain the controlled system, but it could also lead to much higher molecular weight due to the coupling effect [Wu, 1999].

4.4 Kinetic discussion of end-capping

To compare the chain propagation and end-capping rates, a well-defined system was applied to minimize the side reactions occurring in the polymerisation. Table 4-8 shows the experimental procedure and the results.

Table 4-8: End-capping with silyl enol ether 3—kinetic discussion

Monomer	Lewis acid & Additive	SEE[α)]	Temp[β)] °C	M:I:SEE[γ)]	M_n	PD	DP_m[φ)]	Fn[δ)] %	Conversion[ε)] %
iBVE	$SnCl_4$ / *n*-Bu_4NCl	None	-78	10:1:0	1370	1.10	13.33	-	100
		3		20:1:1	2670	1.11	25.92	70.4	98.5
		3		30:1:1	4080	1.10	40.10	56.5	100
		3		10:1:2	1610	1.14	15.43	48.4	90.9
		3		10:1:3	1350	1.14	12.77	50.8	75.8
		3		10:1:4	1100	1.13	10.27	60.9	63.5
		3		10:1:5	910	1.11	8.30	73.0	40.9

Polymerisation time is 5 minutes. Initial monomer concentration: [iBVE]=0. 27 mol L^{-1}

α): Silyl enol ether being applied in polymerisation

β): Polymerisation temperature

γ): General initial initiation ratio is [iBVE]:[IBVE-HCl]:[$SnCl_4$]:[*n*-Bu_4NCl]=10:1:1:0.5:0.75

φ): Relative degree of polymerisation for monomer. The influence of methoxy chain end and ketone chain end from the functionalisation of **SEE 3** are excluded in the calculation. The value is based on SEC analysis.

δ): Chain end functionalities are obtained from integration of proton NMR of the applicable samples

ε): Monomer conversions are obtained by comparing the oligomer yield and initial monomer amount plus initiator amount

4.4.1 Discussions on the current initiation system

Kennedy and Ivan summarized the evidence for relatively slow initiation as follows:[Kennedy, 1991]

Molecular weight distributions are broader than Poisson. (PD>1.1)

Initiation efficiencies are lower than 100%, $I_{eff} = (W_P/M_n)/I_0$,

M_n is higher than theoretical

Nonlinear M_n versus W_p plots, or it running above the theoretical line

Where the I_{eff} is the initiation efficiency, W_p is the weight of polymer, I_0 is the initiator amount.

For the first sample in table 4-8, the degree of polymerisation obtained from proton NMR is 13.3, which is higher than the expected theoretical value of 11 at the 100% monomer conversion. This result gives the initiation efficiency of 83%. Table 4-8 also lists the obtained M_n of this sample as 1370 which is also higher than the

theoretical value of 1100. A plot of M_n versus W_p could not be given here but still these evidence obtained indicates a relatively slow initiation in the current initiation system.

The polymerisations were run on a cooling bath carrousel under anhydrous conditions and a nitrogen atmosphere, under the same polymerisation condition except for different initial ratios of monomer to initiator and **SEE 3**. 7 polymerisations are presented in table 4-8, including a control polymerisation without end-capping, two polymerisations with the end-capping by **SEE 3** at the increased initial monomer amount and 4 polymerisations with increase **SEE 3** amount.

4.4.2 Discussions on end-capping

The effect of increasing monomer to initiator and silyl enol ether ratio on M_n is shown in Figure 4-27. As expected, increasing this ratio produces an increasing M_n. However, the polydispersities of the oligomer samples remain constant. This latter observation is further evidence that end-capping occurs at a timescale that is slower than the propagation process; propagation that is similar to capping would result in the increasing molecular weight distributions of the oligomer samples with end-capping than the oligomer sample polymerised in the absence of end-capping agents.

Compared with the control polymerisation without end-capping, the experimental results indicate that the presence of **SEE 3** has little effect on the initiation process and according to NMR and SEC analysis results the number of oligomer chains in these three polymerisations in figure 4-27 is about the same. The results also indicate that **SEE 3** does not interrupt the chain propagation at these initial concentration ratios and allows the consumption of the monomer.

Figure 4-28 is the MALDI-TOF mass spectrum of OiBVE sample polymerised with the increased relative monomer amount. The spectrum further confirmed the high chain end functionality obtained from the end-capping with **SEE 3**.

From the sample without end-capping the degree of polymerisation obtained from proton NMR is 13.3, which is higher than the expected theoretical value of 11.0 This result indicates that the initiation efficiency in the current initiation system is 83%. As mentioned, the first three polymerisations in table 4-8 look like quasi-living polymerisations in which additional initiation, chain transfer and other termination could be ignored. It indicates a weak end-capping from **SEE 3**. The final 4 polymerisation data in table 4-8 proved the influence that **SEE 3** could have in the

polymerisations. In contrast to the first three polymerisations, the monomer to initiator ratio was maintained at 10:1 in the last 4 polymerisations and the initial amounts of **SEE 3** were increased from 2 to 5 equivalents.

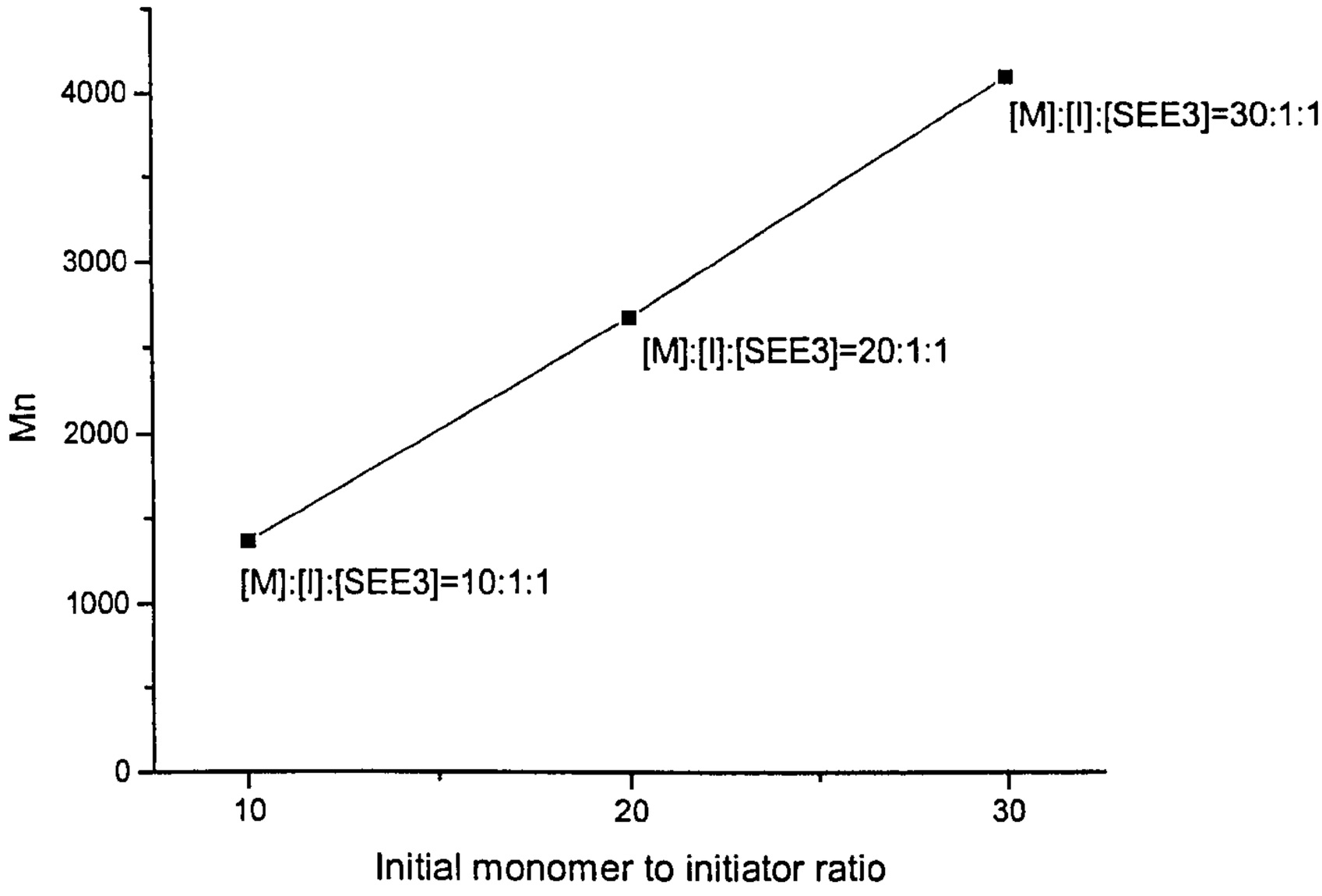


Figure 4-27: Increase of initial monomer amount in end-capping with SEE 3

Initial monomer concentration: [iBVE]=0.27 mol L^{-1}, polymerisation temperature: -78°C,

polymerisation time: 5 minutes

Figure 4-29 is based on the last 4 sets of polymerisation data in table 4-8 when the initial **SEE 3** concentration is increased proportionally. It can be seen that the monomer conversion is proportional to the oligomers' molecular weight in these four polymerisations. When the ratio of monomer to **SEE 3** was decreased, the molecular weight of the oligomer decreased, as expected. One more equivalent of **SEE 3** leads to a 17% reduction in the molecular weight as well as the reduction of monomer conversion. Increased initial silyl enol ether concentration affected the degree of polymerisation.

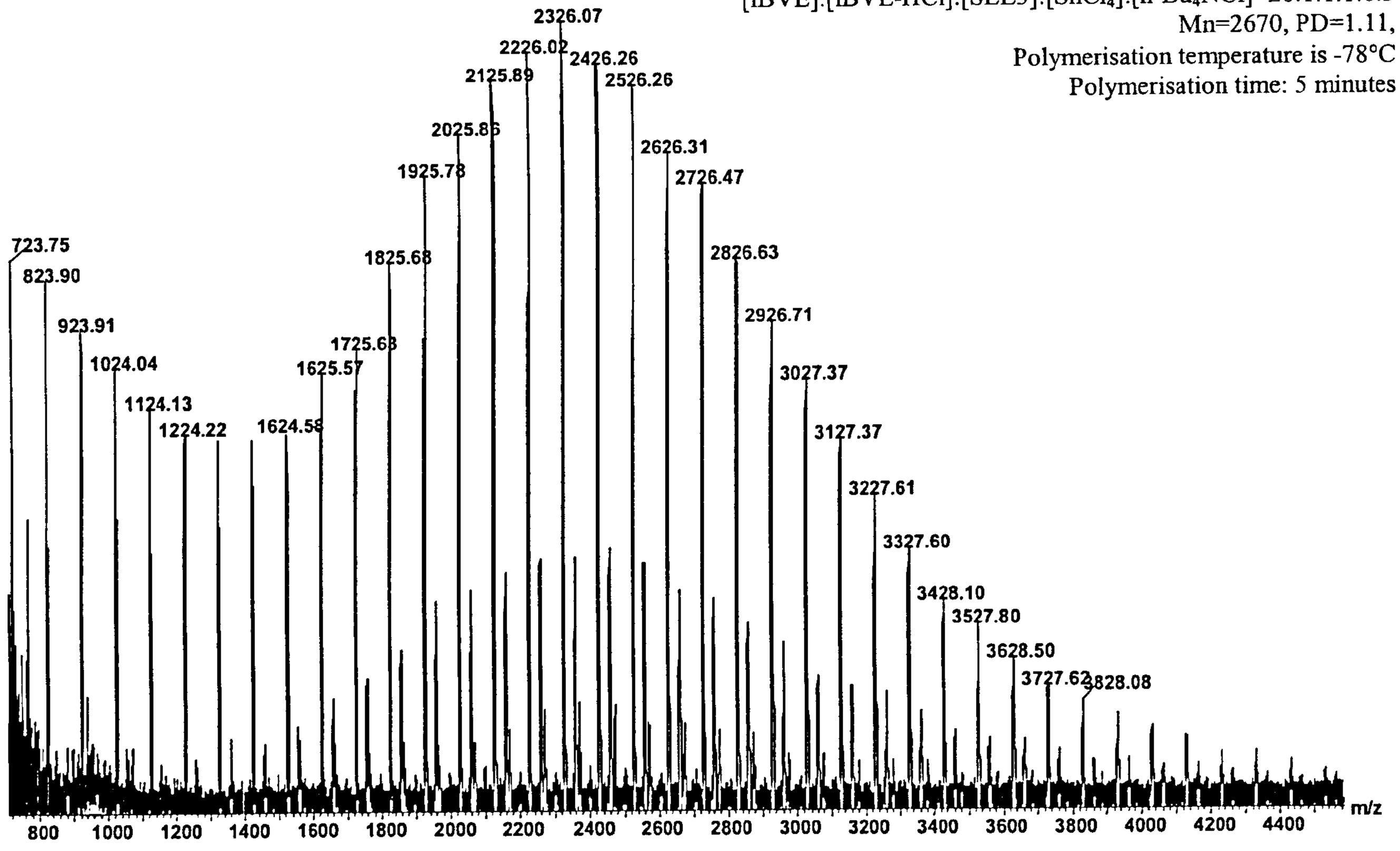


Figure 4-28: MALDI-TOF mass spectrum of OiBVE functionalised by SEE 3 (Initial [iBVE]=0.27mol L^{-1})

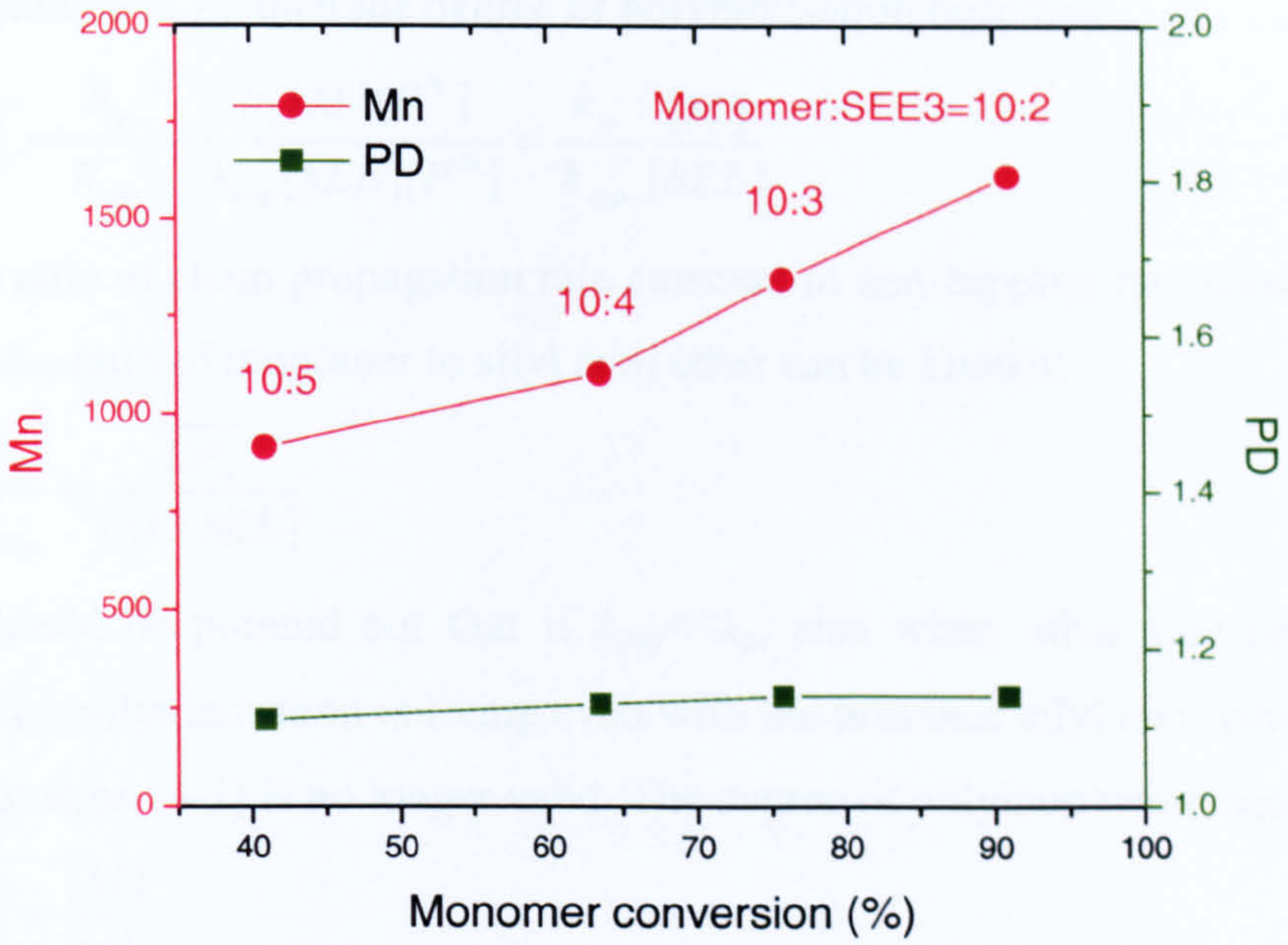


Figure 4-29: Increase of initial SEE 3 concentration in the polymerisation

Initial [iBVE]=0.27 mol L^{-1}, [iBVE]:[iBVE-HCl]:[$SnCl_4$]:[*n*-Bu_4NCl] =10: 1: 0.5:0.75, polymerisation temperature: -78°C, polymerisation time: 5 minutes

In the *ab initio* chain end functionalisation during cationic polymerisation, after initiation of the polymer chain, chain propagation and end-capping rates can be expressed as:

$$R_p = k_p[M][P^{\oplus}]$$

$$R_{cap} = k_{cap}[SEE][P^{\oplus}]$$

R_p: chain propagation rate

R_{cap}: end-capping rate

k_p: chain propagation rate constant

k_{cap}: end-capping rate constant

$[M]$: monomer concentration

$[SEE]$: silyl enol ether concentration

$[P^{\oplus}]$: concentration of carbocationic polymer chain end

$\overline{DP_n}$: degree of polymerisation

Chain termination and other side reactions occur in competition with chain propagation and end-capping. When the side reactions and termination are negligible, the reaction, without end capping, becomes a living polymerisation. Suppose the only

termination reaction occurred in the polymerisation is end-capping reaction, and that k_{cap} is comparable to k_p, then the degree of polymerisation becomes:

$$\overline{DP_n} = \frac{R_p}{R_{cap}} = \frac{k_p[M][P^{\oplus}]}{k_{cap}[SEE][P^{\oplus}]} = \frac{k_p}{k_{cap}}\frac{[M]}{[SEE]} \qquad \textbf{(4-1)}$$

The ratio of chain propagation rate constant to end-capping rate constant can be obtained if the ratio of monomer to silyl enol ether can be known:

$$\frac{k_p}{k_{cap}} = \frac{\overline{DP_n}}{[M/SEE]} \qquad \textbf{(4-2)}$$

It should be pointed out that if $k_{cap} << k_p$, also when other side reactions are negligible, the polymerisation is living even with the presence silyl enol ethers. In such a system, equation (4-1) is no longer valid. The degree of polymerisation becomes:

$$\overline{DP_n} = \frac{[M]}{[I]} \qquad \textbf{(4-3)}$$

However, when k_{cap} and k_p are comparable the system is not living, equation (4-1) can also become:

$$\overline{DP_n} = \frac{K}{[SEE]} \qquad \textbf{(4-4)}$$

where $K = \dfrac{k_p[M]}{k_{cap}}$

Because of the different rates of monomer and silyl enol ether consumption, only the initial $[M]$ and $[SEE]$ can be certain. At very low monomer conversion $[M]$ and $[SEE]$ can be regarded as constant, in such a case an increase in $[SEE]$ will lead to the proportional decrease of DP_n. It was difficult to control the monomer conversion rate to less than 5% due to the very high cationic polymerisation rate.

However even the monomer conversion rates were not controlled to be low enough, a plot of DP_n versus initial silyl enol ether concentration is still shown in figure 4-30. These 4 parallel polymerisations presented in the figure were run at the presence of different amount of silyl enol ether 3. It can be seen from the figure that increase of the initial silyl enol ether 3 concentration indeed leads to the decrease of degree of polymerisation, this seems to indicate that equation 4-4 can be used to describe the polymerisation and chain end functionalisation procedure.

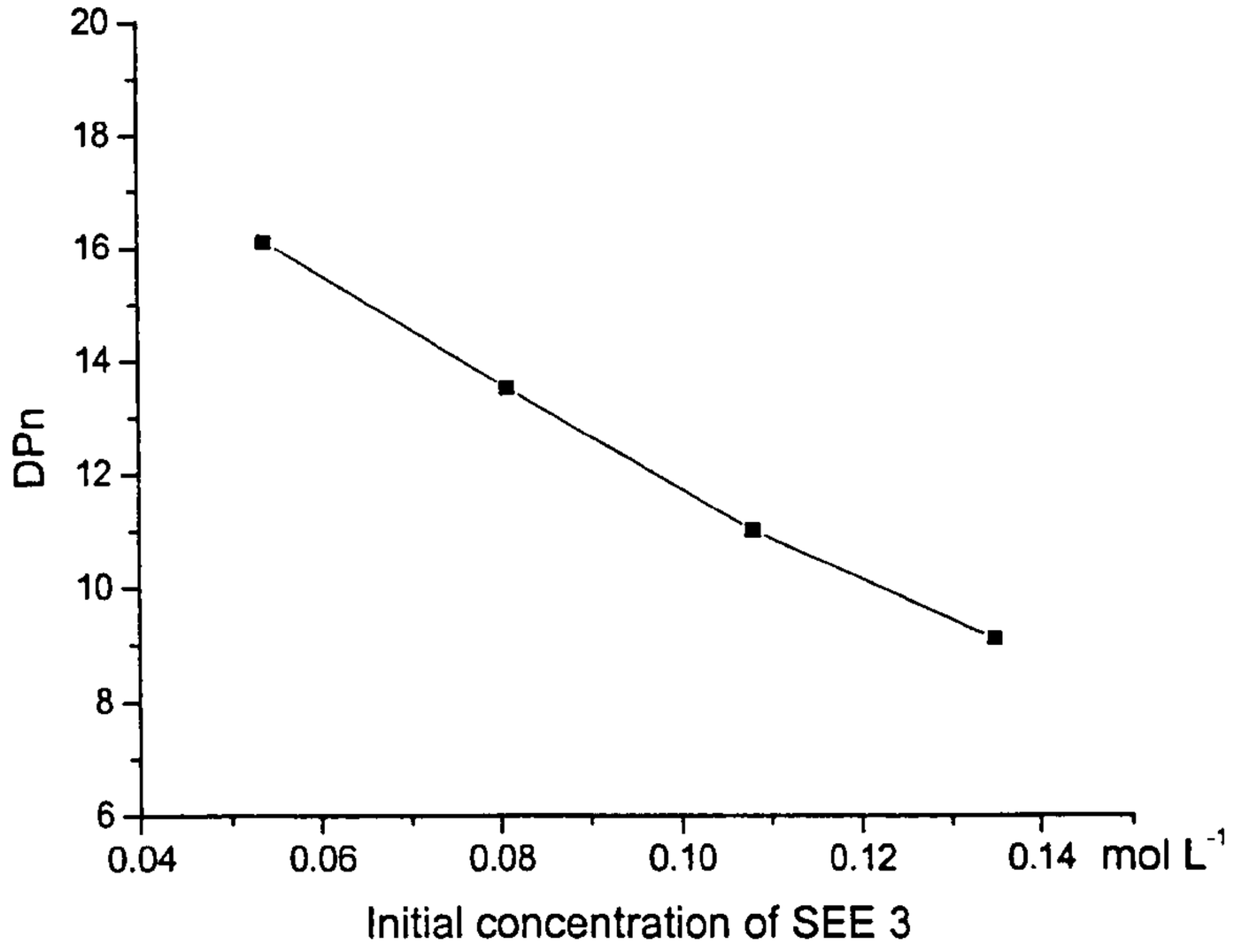


Figure 4-30: Increase of initial silyl enol ether concentration in the *ab initio* polymerisation

Initial [iBVE]=0.27 mol L^{-1}, [iBVE]:[iBVE-HCl]:[$SnCl_4$]:[*n*-Bu_4NCl]=10:1:0.5:0.75, polymerisation temperature:-78°C, polymerisation time: 5 minutes

4.5 The effect of polymerisation temperature on end-capping

Figure 4-31 summarises the chain end functionalities of oligo(isobutyl vinyl ether) and oligo(ethyl vinyl ether) with the end-capping of **SEE 1** and/or **SEE 2**, obtained at different polymerisation temperatures. It can be seen that when $SnCl_4$ was applied as co-initiator, low temperature favours end-capping.

The chain end functionalities were obtained according to the integration of proton NMR spectra of functionalised oligomer samples. Although oligomers were made with low molecular weights to improve the accuracy of chain end functionality analysis, the integration still contained errors due to the integration of weak signals and also overlapped signals, which could not be avoided. On the 250 MHz proton NMR the α-end methyl resonance at 1.1 ppm actually contains three parts: α-end methyl resonance, satellites of the two methyl groups (recorded as signal 6 in the NMR spectra presented in figure 4-6 to 4-10) and satellites of the methylene resonance (recorded as signal 2 in the NMR spectra in figure 4-6 to 4-10). The large resonances from the backbone methyl groups and the methylene group could also affect the baseline of the integration, together with their satellite's influences the obtained α-end methyl

resonance integration values are higher than reality and this decreases the chain end functionalities. This was probably the reason that on figure 4-31 some of the chain end functionalities are low. The fact that the silyl enol ethers capped oligomers at all polymerisation temperatures is shown by the prominent amount of functionalised chain end in MALDI-TOF mass spectral analysis. Low temperature indeed improves the chain end functionality according to MALDI-TOF MS results as well.

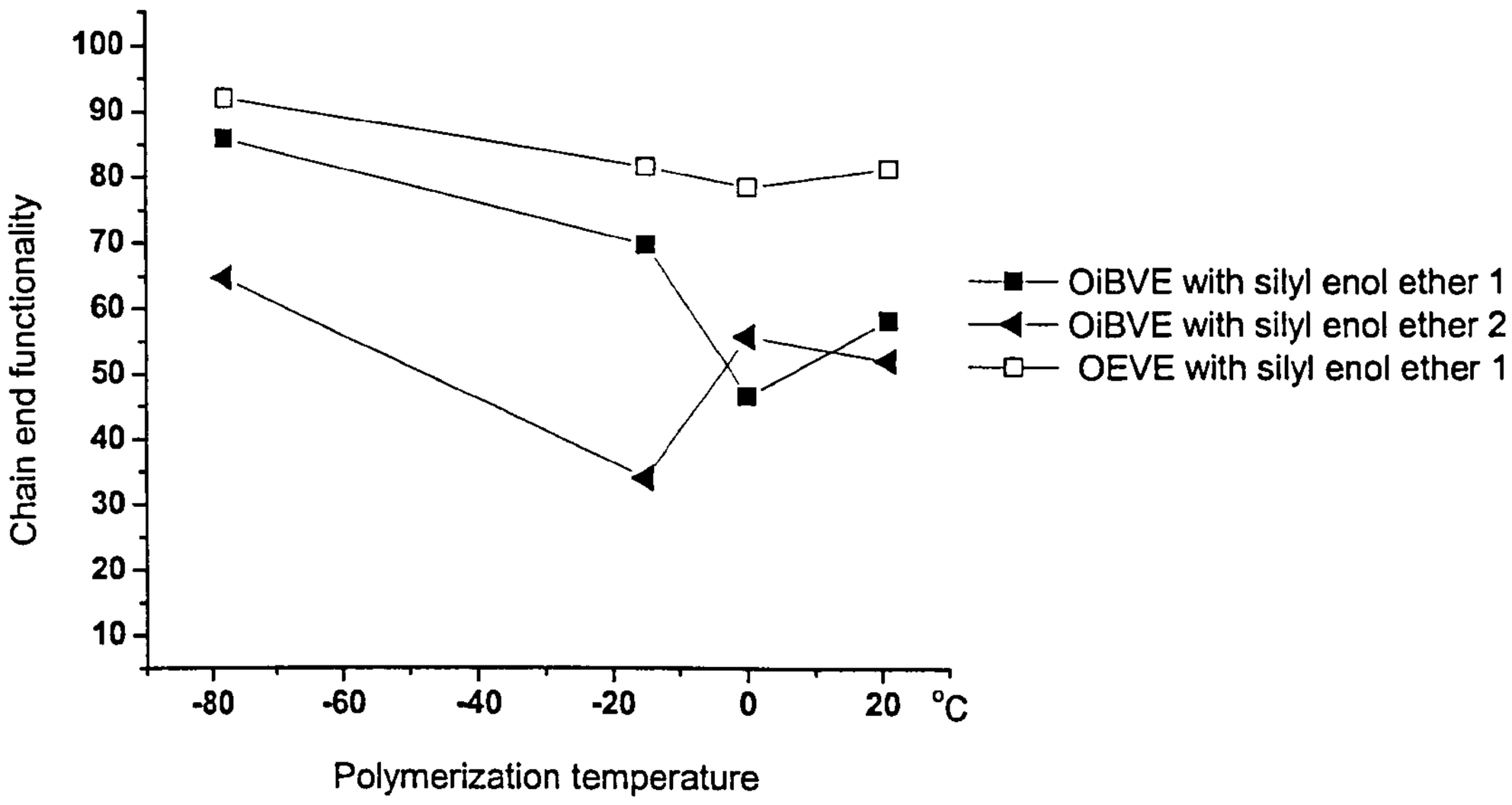


Figure 4-31: Chain end functionalities under different polymerisation temperatures

Initial [iBVE]=[EVE]=0.38 mol L^{-1}, [M]:[iBVE-HCl]:[SEE]:[$SnCl_4$]:[*n*-Bu_4NCl]=10:1:1:0.5:0.75,

polymerisation time: 60 minutes

It seems that polymerisation temperature affects the end-capping, through its affect on the side reactions; end-capping can suppress the majority of them. At room temperature, fast side reactions occurred and for the relatively low reactivity silyl enol ether like, **SEE 4**, end-cappings were seriously reduced.

Table 4-9 summarises the different chain ends observed at different polymerisation temperatures with and without end-capping. Scrutinizing over the table some general facts were found which help to identify the influence of polymerisation temperature in the polymerisation.

Table 4-9: summary of polymerisation temperatures and chain ends

Temperature °C	Control Polymerisation	SEE 1	SEE 2	SEE 3	SEE 4
-78	**1, 7, 6, 3, 5, 4, 8, 7,**	**1-1, 3/1-2**	**2-1, 2-2**	**3-1, 7, 6, 3-2, 3**	**4-1, 1, 7', 6, 3**
-15/*n*-Bu_4NCl	**6, 1, 3, 7', 2' 2, 8, 5, 4**	**1-1, 3/1-2, 7', 5, 2**	**2-1, 2-2, 2-3**	**3-1, 3, 2', 7, 5, 2**	**4-1, 3, 2', 8, 2, 7, 5**
-15	**1, 6, 3, 7, 2', 2, 1, 2, 8**	**1-1, 3/1-2, 6, 8,**	**2-1, 2-2, 6, 2' 3, 8, 7, 1,**	**3-1,2' 3, 6,**	**4-1, 6, 3, 2',**
0	**6, 3, 1, 8, 2', 7, 2, 4, 5**	**1-1, 3/1-2, 2**	**2-1, 2-2, 3, 2', 6**	**3-1 3, 6,**	**4-1, 3, 6, 8**
21	**3, 8, 6, 2, 4,**	**1-1, 3/1-2, 7, 5**	**2-1, 2-2, 3, 6, 8**	**3-1 3**	**3, 4-1**

Ketone chain ends derived from silyl enol ether functionalised chain ends were formed at all temperatures whenever it was applied. The only exception was with the use of **SEE 4** at room temperature. Under these conditions, both oligomer **3** from side reaction and **4-1** from end-capping are dominant.

Oligo (isobutyl vinyl ether) with chain end **3**, which is postulated as a primary hydroxy chain end, widely exists although in small amount in the presence of reactive silyl enol ethers. When the most reactive **SEE 2** was applied at low temperature of -78°C or -15°C in the presence *n*-Bu_4NCl, **3** is not observed. The formation of **3** is probably a fast endothermal reaction and is therefore entropically favoured by high polymerisation temperature.

The diisobutanol chain end is observed at all temperatures in different amounts. In a control polymerisation without end-capping by silyl enol ethers, the diisobutanol chain end is reduced when other side reactions become stronger as a result of the increased polymerisation temperature. When silyl enol ethers are applied in the polymerisation, the diisobutanol chain end is generally largely reduced at all temperatures but the side reactions that produce isobutanol can still be observed in the spectra. For example, isobutanol should be produced as a byproduct of alkene chain end **8**, aldehyde chain end **2**, internal alkene aldehyde chain end **5** and internal alkene methoxy chain end **4**. If the postulation about **3** is right, the formation of this chain end

also releases isobutanol. As we explained before this suppression of diisobutanol chain ends can proceed in two ways: the reactive silyl enol ether can react with the diisobutanol chain end and give a functionalised chain end, or the isobutanol capping is slower than silyl enol ether capping and other side reactions.

At -78°C, the amount of the postulated secondary hydroxy chain end **7'** is higher than **3**. This is in accordance with the first point that low temperature does not favor the formation of **3**. One consideration concerning the formation of **7'** is that it is formed due to an impurity from the quenching procedure. The lower the polymerisation temperature, the more living chain end there is left at quenching and more **1** as well as **7'** are formed.

4.6 Polymerisation of ethyl vinyl ether with the end-capping

4.6.1 Polymerisation of ethyl vinyl ether (EVE)

Oligo(ethyl vinyl ether)—OEVE was synthesised in parallel polymerisation with OiBVE. Table 4-10 compares the polymerisation of EVE and iBVE.

Table 4-10: Comparison of OEVE with OiBVE

Run	Monomer	Lewis acid	Additive	Temperature °C	DP_n	M_n	PD	Conversion %
1	iBVE	$SnCl_4$	None	21	8.7	870	2.24	58.1
	EVE	$SnCl_4$	None	21	12.5	900	3.24	51.6
2	iBVE	$SnCl_4$	None	-15	8.0	800	1.76	57.8
	EVE	$SnCl_4$	None	-15	10.6	760	1.74	75.3
3	iBVE	$SnCl_4$	*n*-Bu_4NCl	-15	7.6	760	1.62	81.8
	EVE	$ZnCl_2$	None	-15	12.1	870	1.60	75.3
4	iBVE	$SnCl_4$	None	-78	9.4	940	1.56	100
	EVE	$SnCl_4$	None	-78	12.5	900	1.19	100

Initial [iBVE]=[EVE]=0.38 mol L^{-1}, [M]:[iBVE-HCl]:[SEE]:[$SnCl_4$]:[*n*-Bu_4NCl]=10:1:1:0.5 :0.75, polymerisation time: 60 minutes

M_n data presented in table 4-10 shows that polymerisation of EVE gives a higher degree of polymerisation than with iBVE. With the repeat unit of 72.11 and the

initial monomer to initiator ratio of 10:1, the expected oligomer's M_n should be around 820 for OEVE and 1100 for OiBVE. We observed that OiBVE has a lower M_n than expected and OEVE has a higher M_n than expected. This higher degree of polymerisation of OEVE indicates a lower initiation efficiency. It is understandable that using iBVE-HCl as initiator, higher initiation efficiency was obtained for iBVE monomer than for the EVE monomer.

Figures 4-32 and 4-33 show expanded MALDI-TOF mass spectra of the OEVE samples. Similar side reactions are observed in the polymerisation of EVE to those observed with iBVE. Alkene and aldehyde chain ends are observed on the MALDI-TOF mass spectra. Because oligomer ions with diethanol chain ends have the same mass as primary hydroxy chain ends, it is difficult to state which is observed, it's probable that both of them contribute to this signal. Table 4-11 lists some of the different chain ends observed in polymerisation of EVE. Side reactions due to additional initiation are observed in the polymerisations (these are also listed in table 4-11 but will be discussed separately).

Table 4-11: Different chain end observed in polymerisation of EVE

number	Initiator	OEVE with different α or ω-ends	OEVE mass* *m/z*	
			Theoretical	Experimental
E-1	iBVE-HCl	$CH_3CH(OiBu)\text{-}(EVE)_{10}\text{-}OCH_3/Na^+$	875.52	875.87
E-2		$CH_3CH(OiBu)\text{-}(EVE)_{10}\text{-}OC_2H_5\ /Na^+$	889.53	889.77
E-3		$CH_3CH(OiBu)\text{-}(EVE)_{10}\text{-}CH{=}CH(OiBu)\ /Na^+$	915.55	915.86
E-4		$CH_3CH(OiBu)\text{-}(EVE)_{10}\text{-}CH_2CHO/Na^+$	887.55	887.78
E-5		$CH_3CH(OiBu)\text{-}(EVE)_{10}\text{-}CH_2CH_2OH/Na^+$	889.56	889.77
E-5'		$CH_3CH(OiBu)\text{-}(EVE)_{10}\text{-}CH_2CH_2OH/H^+$	867.55	867.78
E-6	Water	$H\text{-}(EVE)_{10}\text{-}OCH_3/Na^+$	847.43	847.96
E-7		$H\text{-}(EVE)_{10}\text{-}OC_2H_5\ /Na^+$	861.44	861.95

*Isotope oligomer ion mass were calculated and picked up for theoretical and experimental values.

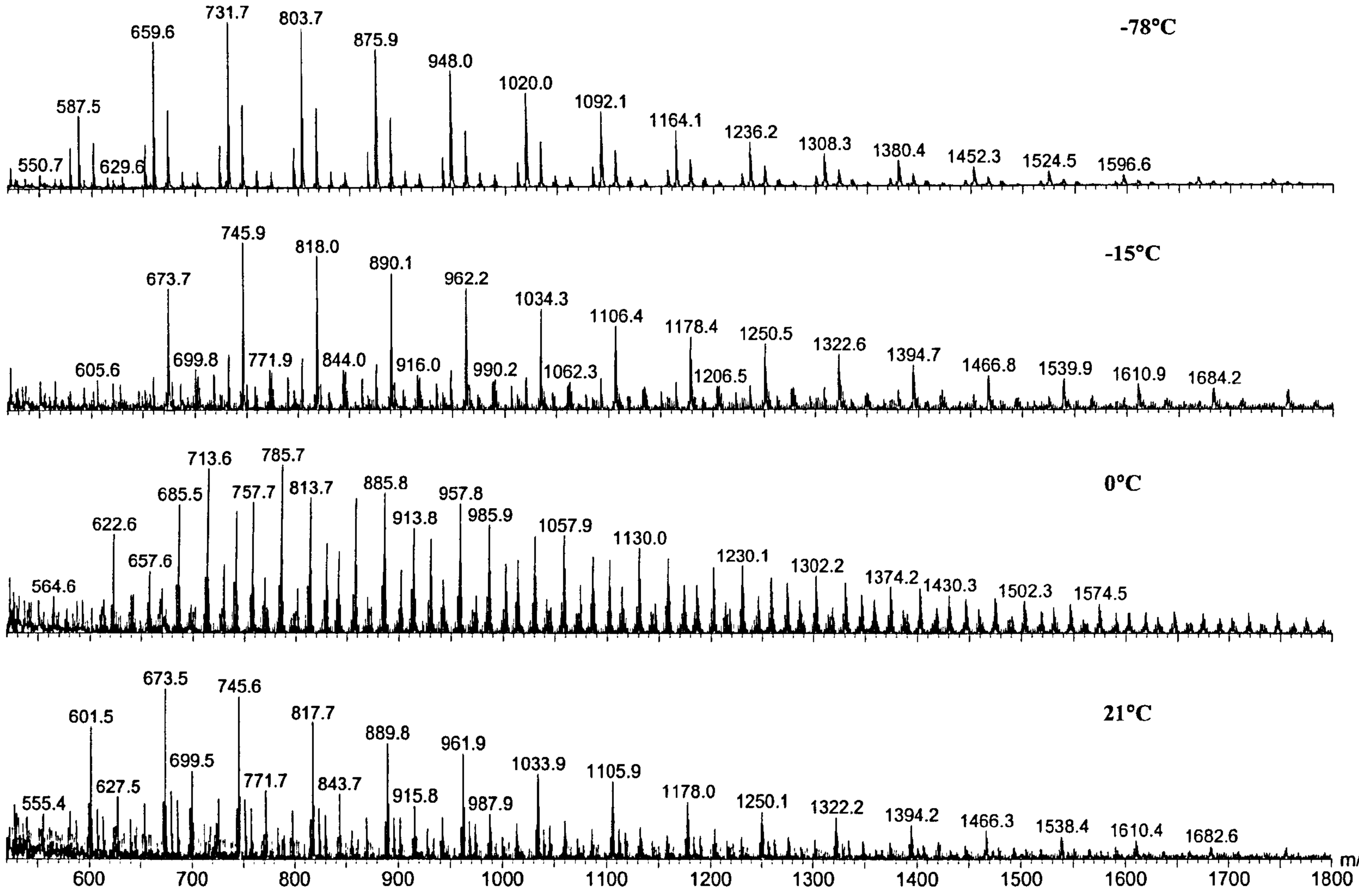


Figure 4-32: MALDI-TOF mass spectra of OEVEs polymerised at different temperatures without end-capping

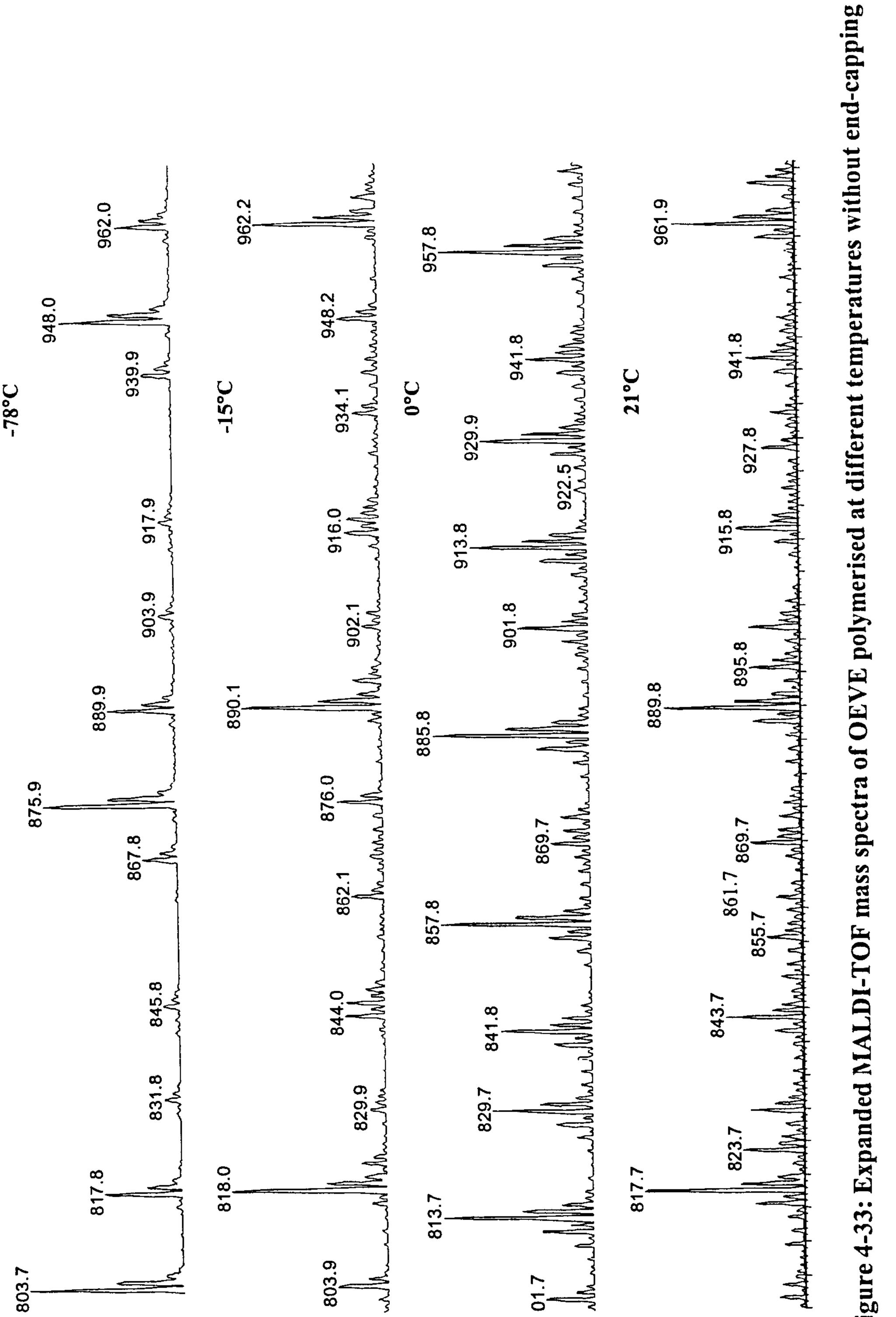


Figure 4-33: Expanded MALDI-TOF mass spectra of OEVE polymerised at different temperatures without end-capping

At low temperature, the polymerisation of EVE has more living chain end left at 60 minutes for the quenching reaction with methanol compared to the polymerisation of iBVE. Also, OEVE has a slightly narrower PD than OiBVE at low temperature (-78°C) although at room temperature, PD of OEVE is broader than OiBVE. Figure 4-33 is the proton NMR of OEVE with the assignments.

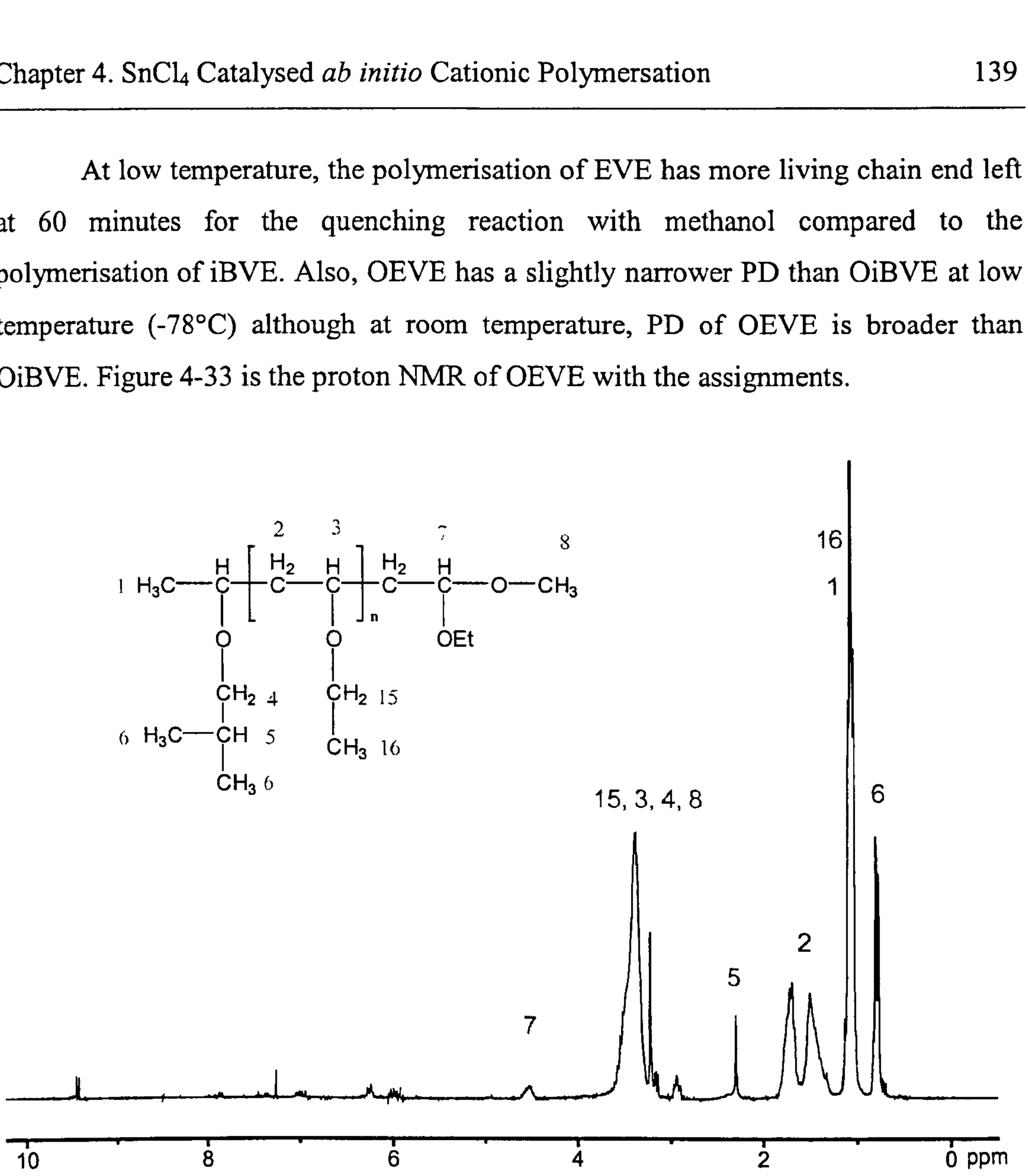
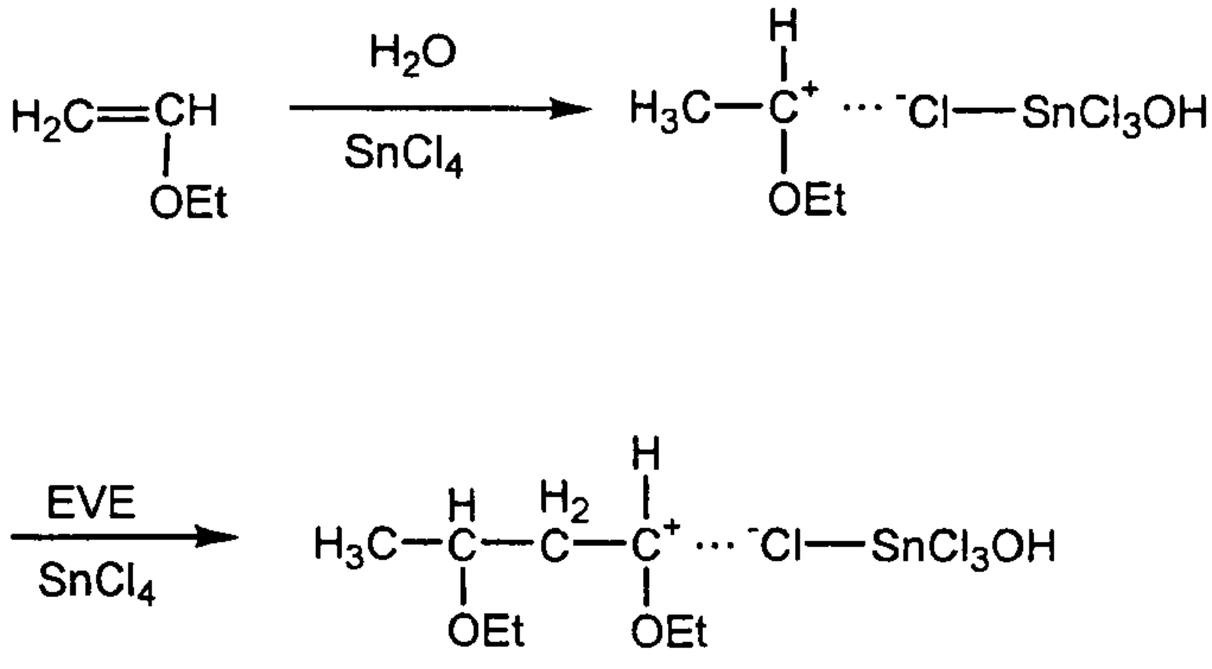


Figure 4-34: ^{1}H NMR of OEVE

Initial [EVE]=0.38 mol L^{-1}, [EVE]:[iBVE-HCl]:[$SnCl_4$]=10:1:0.5, polymerisation temperature: -78°C, polymerisation time: 60 minutes

4.6.2 Evidence of water initiation

It is hard to distinguish water initiation in the polymerisation of iBVE because water initiation gives the same α-end structure as iBVE initiation. In the polymerisation of EVE, however, water initiation gives a different α-end structure that can be observed in the MALDI-TOF mass spectra of OEVE. The mechanism of water initiation is shown in scheme 4-11 [Katayama, 2001].



Scheme 4-11: Water initiation in polymerisation of EVE

Table 4-11 lists two observed OEVE in the water initiated α-end. Oligomer ions due to water initiation are only present in very small amounts but they are observed in OEVE, synthesised at all temperatures except -78°C. At this low temperature, water initiation seems to be suppressed.

4.6.3 End-capping with **SEE 1** in the polymerisation of EVE

Table 4-12 compares the SEC results for polymerisation of EVE with end-capping with **SEE 1** and the control polymerisation without end-capping.

Table 4-12: End-capping with SEE 1 in the polymerisation of EVE

Run	Monomer	Lewis acid	Additive	SEE	Temp °C	M_n	PD	Fn %	Conversion %
1	EVE	$SnCl_4$	None	None	21	900	3.24	-	51.6
		$SnCl_4$		1	21	930	3.4	81.2	71.6
2		$SnCl_4$		1	0	710	2.48	78.4	87.3
3		$SnCl_4$	None	None	-15	760	1.74	-	75.3
		$SnCl_4$		1	-15	710	2.57	81.6	61.8
4		$ZnCl_2$		None	-15	870	1.6	-	75.3
		$ZnCl_2$		1	-15	660	2.54	97.0	93.5
5		$SnCl_4$		None	-78	900	1.19	-	100
		$SnCl_4$		1	-78	740	2.75	92.0	100

Initial [EVE]=0.38 mol L^{-1}, [EVE]:[iBVE-HCl]:[SEE]:[$SnCl_4$]:[*n*-Bu_4NCl]=10:1:1:0.5:0.75, polymerisation time: 60 minutes

End-capped OEVE samples have broader PD and lower M_n than corresponding OEVE samples without end-capping. High chain end functionality was observed (table 4-12) and this shows the high end-capping reactivity of **SEE 1** in the polymerisation of EVE. Figure 4-35 shows the proton NMR spectrum of the **SEE 1** functionalised OEVE sample. Chain end functionality of the sample is calculated by comparing the ω-end aromatic integration and the integration of the two α-end methyl groups' resonances (assigned as signal 6 in figure 4-35).

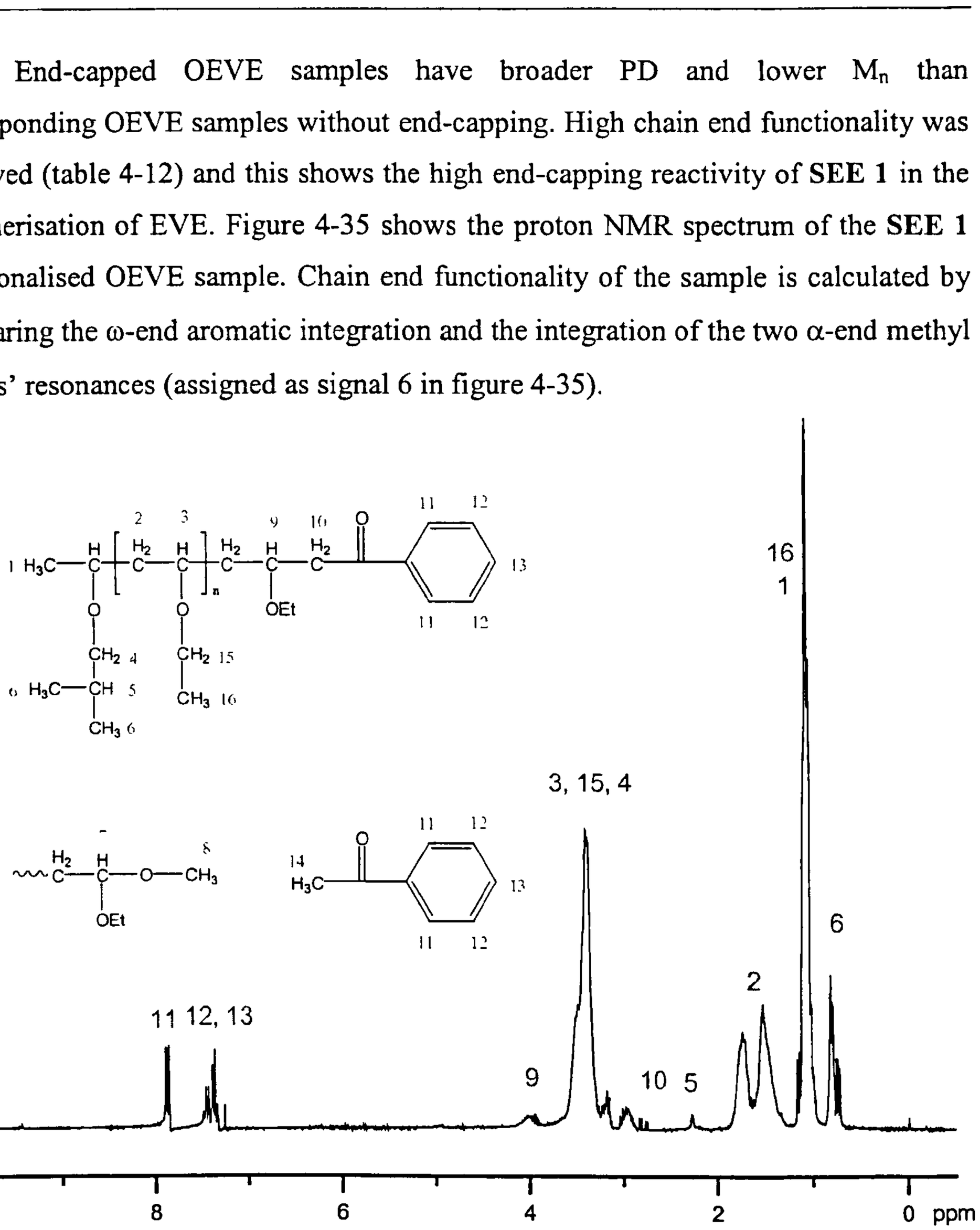


Figure 4-35: ^{1}H NMR spectrum of functionalised OEVE

Initial [EVE]=0.38 mol L^{-1}, [EVE]:[iBVE-HCl]:[SEE 1][$SnCl_4$]=10:1:1:0.5, polymerisation temperature: -78°C, polymerisation time: 60 minutes

Figure 4-36 and 4-37 show the full and expanded MALDI-TOF spectra of end-capped OEVE samples obtained at different temperatures. Table 4-13 lists the observed **SEE 1** functionalised OEVE . Clearly, the majority of chain ends are functionalised at all polymerisation temperatures. Generally, OEVE reacts to give a higher amount of chain end functionalities compared to OiBVE. At room temperature, oligomer **E-1-1**, **E-1-2**, **E-1-3**(or **E-1-4**) and **E-1-5** (or oligomer **E-2** or **E-6** in table

4-11) are observed together with limited chain ends from side reactions (figure 4-37). At other temperatures, **E-1-1**, **E-1-2** and **E-1-3** were formed and exclusively observed.

Table 4-13: Observed functionalised OEVE

number	Initiator	OEVE with different α or ω-ends	OEVE mass* *m/z*	
			Theoretical	Experimental
E-1-1	iBVE-HCl	$CH_3CH(OiBu)$-$(EVE)_{10}$-CH_2-C(=O)-Ph /Na^+	963.64	963.83
E-1-2		$CH_3CH(OiBu)$-$(EVE)_9CH_2CH$=CHC(=O)Ph /Na^+	917.53	917.78
E-1-3		$CH_3CH(OiBu)$-$(EVE)_9CH_2CH(OH)CH_2$C(=O)Ph /Na^+	935.54	935.76
E-1-4	Water	H-$(EVE)_{10}$- CH2-C(=O)-Ph /Na^+	935.55	935.76
E-1-5		H-$(EVE)_{10}$-CH2-CH=CH-C(=O)-Ph /Na^+	889.44	889.66

Experimental values are based on the detailed 21°C OEVE MALDI-TOF mass spectrum on figure 4-37. Oligomer **E-3** and **E-4** are both listed because they have the similar theoretical values, which is near the observed experimental value, * Isotope molecular mass is calculated.

4.7 Polymerisation of methyl vinyl ether and the end-capping

Due to the lower critical solution temperature property of aqueous solution of the oligo (methyl vinyl ether), it has recently been applied as a segment in block copolymers that are thermally responsive smart polymer materials [Aoshima, 1995]. OMVE was synthesised at -78°C under anhydrous conditions and a nitrogen atmosphere. $SnCl_4$ was added as a Lewis acid. Table 4-14 shows data for the polymerisation of OMVE with end-capping by **SEE 3**.

Table 4-14: Polymerisation of OMVE and the end-capping with SEE 3 and SEE 4

Run	Monomer	Lewis acid	Additive	SEE	M:I:SEE	M_n	PD	Fn/%	Conversion/%
1				None	10:1:0	225	1.92	-	30.4
2	MVE	$SnCl_4$	*n*-Bu_4NCl	3	10:1:1	569	1.50	N/A*	48.8
3				4	10:1:1	1464	1.57	N/A*	76.0

[MVE]:[iBVE-HCl]:[SEE]:[$SnCl_4$]:[*n*-Bu_4NCl]=10:1:1:0.5:0.75, Polymerisation was carried out at -78°C for 45 minutes. * Quantitative proton NMR analysis is not applicable due to the overlapping of α-end proton resonances and ω-end proton resonances.

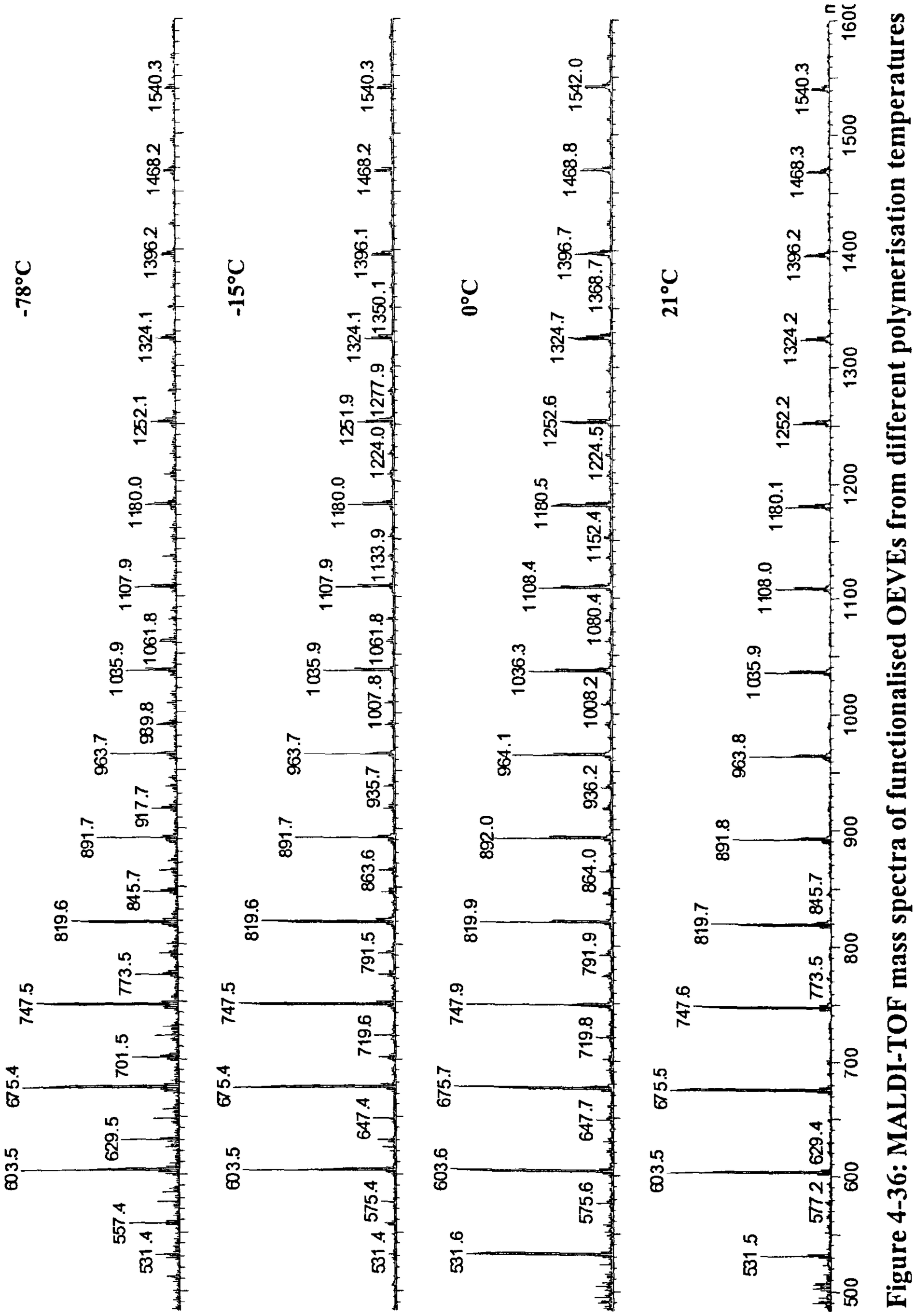


Figure 4-36: MALDI-TOF mass spectra of functionalised OEVEs from different polymerisation temperatures

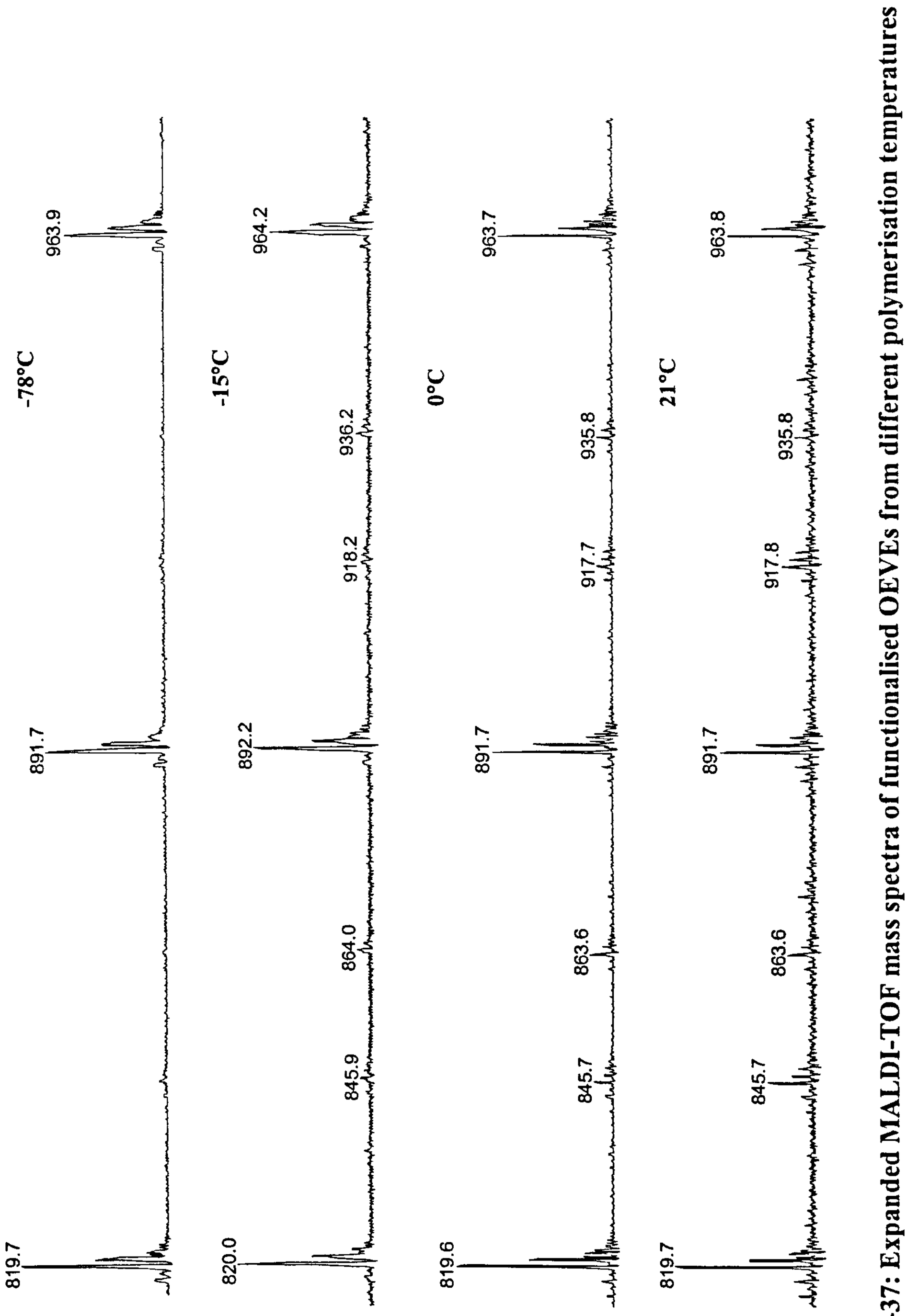


Figure 4-37: Expanded MALDI-TOF mass spectra of functionalised OEVEs from different polymerisation temperatures

As introduced in chapter 2, the polymerisation solutions were washed with warm water to remove the Lewis acid and added salt and recover OMVE (OMVE is insoluble in hot water). The boiling point of DCM, the polymerisation solvent, is 40°C therefore it was necessary to use water < 40°C for the washing procedure to avoid loss of this oligomer during recovery procedure. This could have affected the monomer conversion because it was calculated according to oligomer yield. The monomer conversions in table 4-14 are low.

Control polymerisation of MVE without end-capping gives a oligomer with low M_n and broad PD. Polymerisations in the presence of **SEE 3** and **SEE 4** give higher M_n and narrower PDs. The theoretical molecular weight of this polymer should be 681 g mol^{-1}, which is one iBVE initiator mass plus 10 MVE mass. Table 4-14 illustrates that the M_n of control polymerisation was apparently much lower than theoretical M_n.

In the presence of **SEE 3**, the oligomer chain length obtained is reasonable. ESI MS (Figure 4-38) shows two predominant series of oligomers , they are methoxy and **SEE 3** functionalised ketone chain ends respectively.

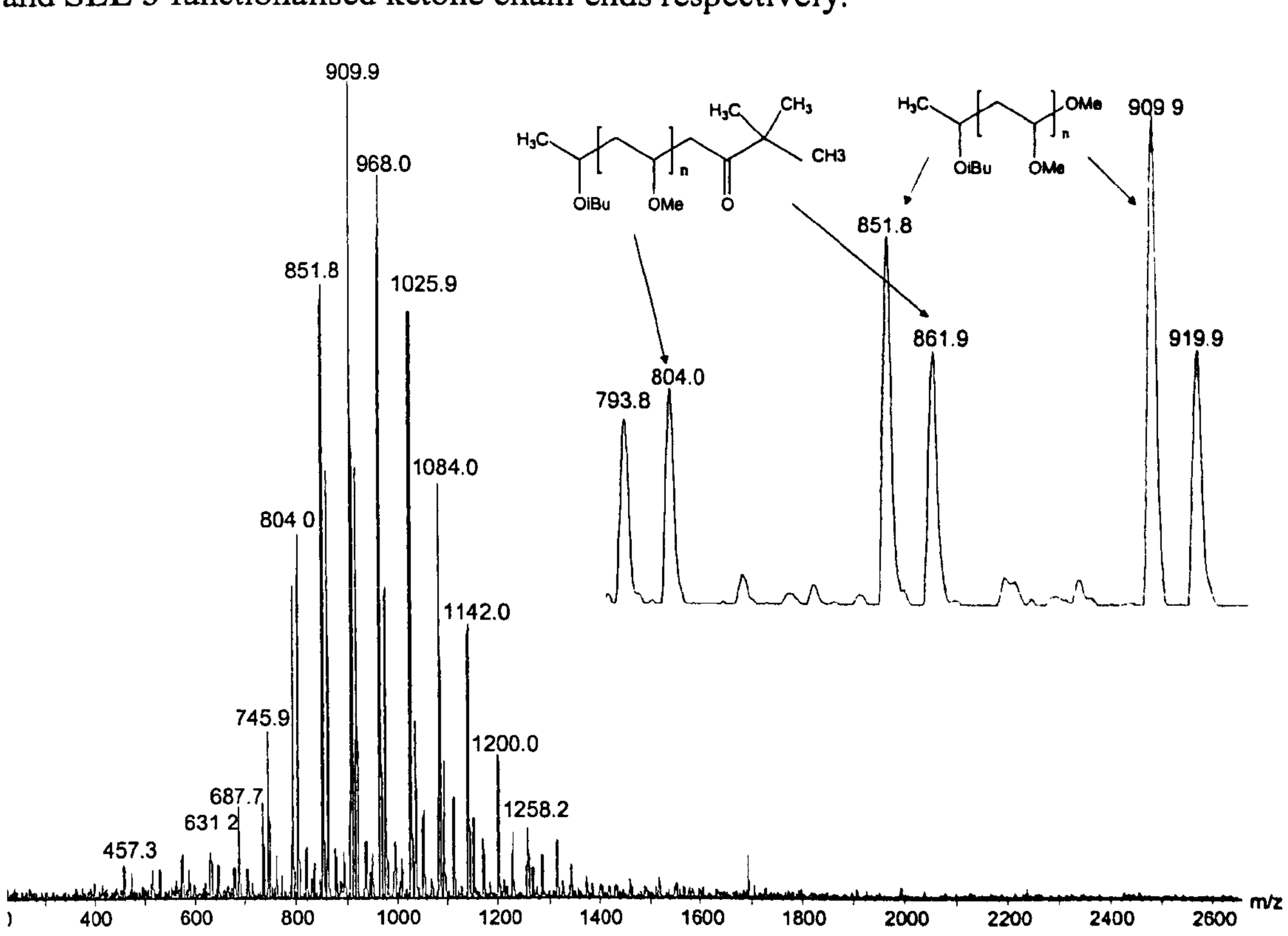


Figure 4-38: LC-ESI MS of OMVE end-capped by SEE 3

Figure 4-39 and figure 4-40 shows the proton NMR spectra of OMVE without and with the end-capping of **SEE 3**. In figure 4-40 the enhanced resonance at ~1.1ppm compared with figure 4-39 gives further evidence of the chain end functionalisation by the capping with **SEE 3**.

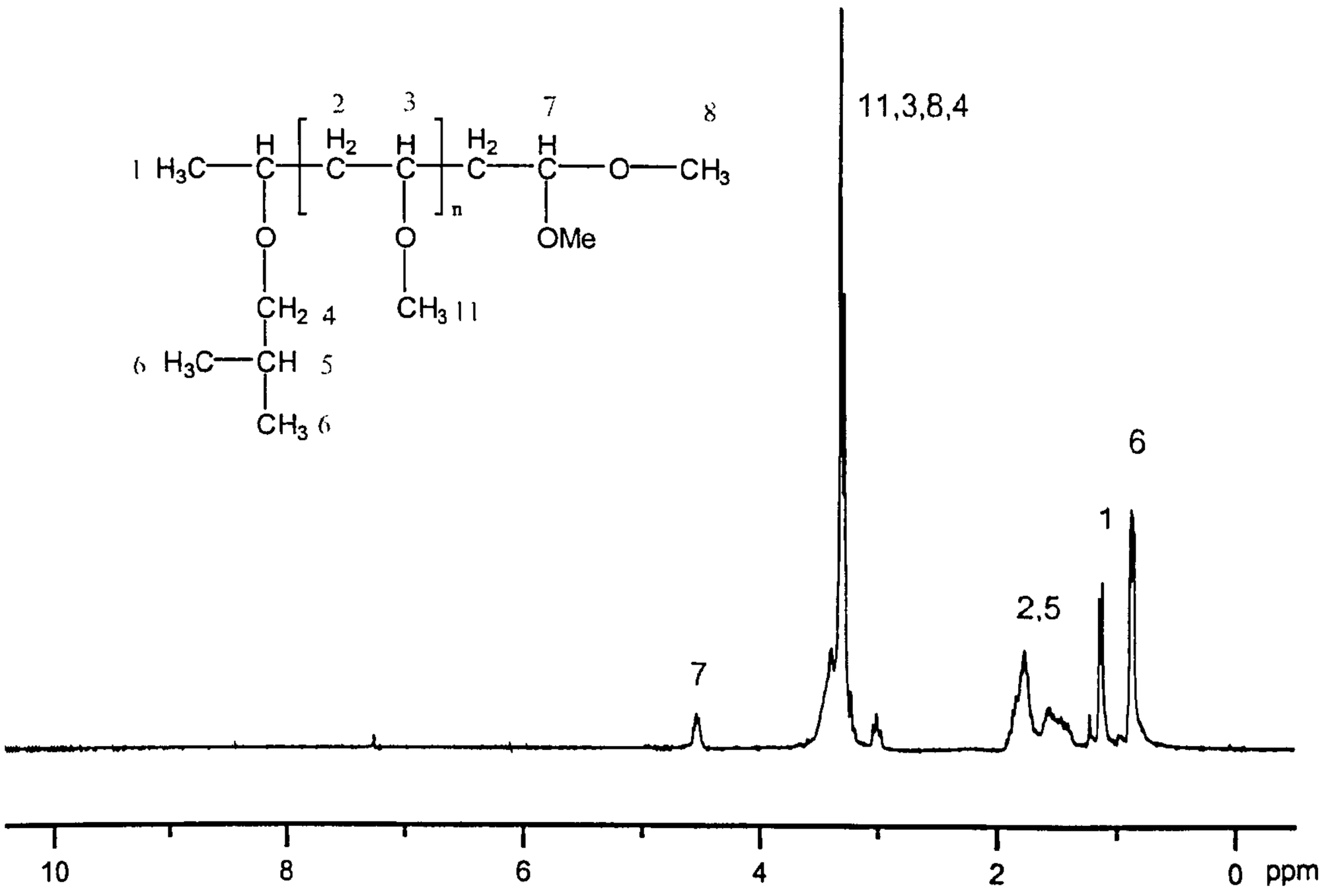


Figure 4-39: ^{1}H NMR of OMVE without end-capping

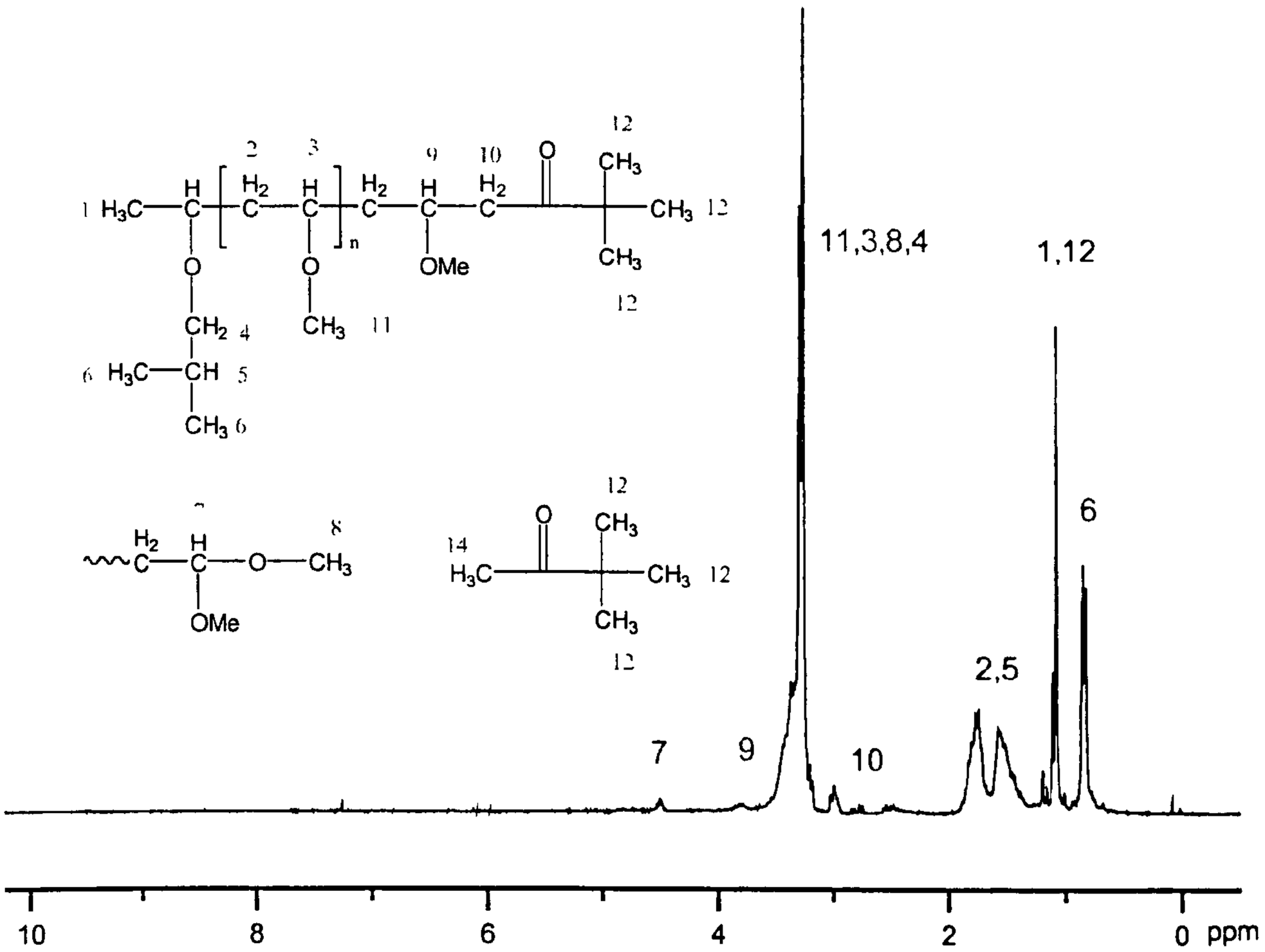


Figure 4-40: ^{1}H NMR of OMVE end-capped by SEE 3

SEE 4 had a significant effect on the polymerisation and gave OMVE with higher molecular weight. It was formerly observed that in the polymerisation of iBVE at the same polymerisation temperature, **SEE 4** gave low chain end functionality but longer oligomer chains. Figure 4-41 shows the MALDI-TOF mass spectrum of OMVE with the end-capping of **SEE 4**. It shows the symmetrical distribution of long polymer chain with the methoxy chain end. Silyl enol ether capped chain ends are not observed. The polymerisation in the presence of **SEE 4** shows enhanced chain propagation and less side reactions.

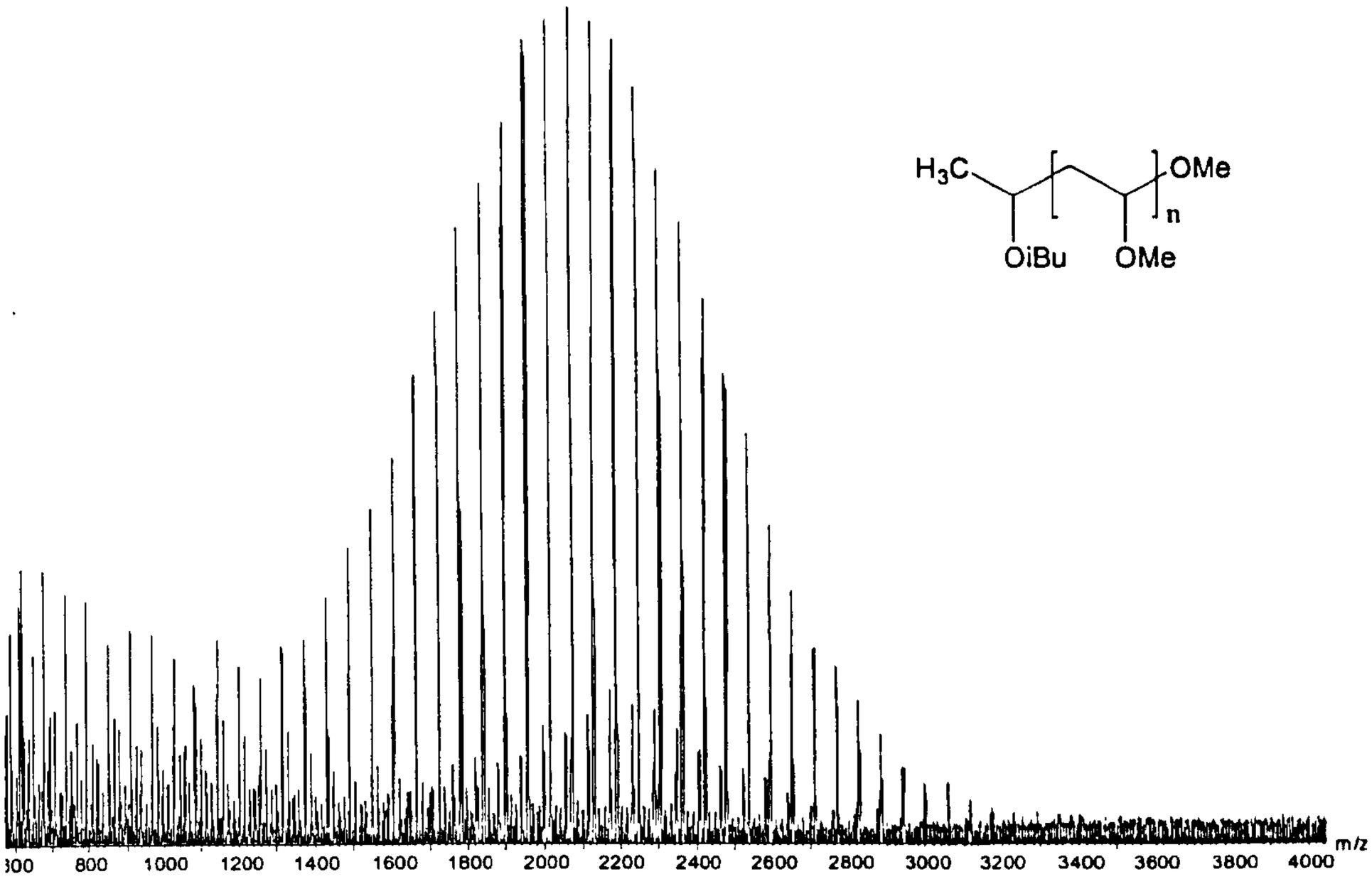


Figure 4-41: MALDI-TOF mass spectrum of OMVE polymerised in the presence of SEE 4

[MVE]:[iBVE-HCl]:[SEE]:[$SnCl_4$]:[*n*-Bu_4NCl]=10:1:1:0.5:0.75, Polymerisation was carried out at -78°C for 45 minutes.

Table 4-15 is the summary of the OMVE chain ends observed.

Table: 4-15: Various OMVE chain ends being observed

number	Initiator	OMVE with different α or ω-ends	OMVE mass* *m/z*	
			Theoretical	Experimental
M-1	iBVE-HCl	$CH_3CH(OiBu)$-$(MVE)_{12}$-OCH_3 /Na^+	851.7	851.8
M-3-2		$CH_3CH(OiBu)$-$(MVE)_9CH_2CH=CHC(=O)C(CH_3)_3$ /Na^+	829.7	829.6
M-3-1		$CH_3CH(OiBu)$-$(MVE)_9CH_2C(=O)C(CH_3)_3$ /Na^+	803.6	803.8
M-2		H-$(MVE)_{10}$- OCH_3 /Na^+	1970.3	1970.2
M-3	Water	H-$(MVE)_{10}CH_2$-CHO/Na^+	821.6	821.8
M-4		H-$(MVE)_{10}CH_2$=CH-OMe/Na^+	835.6	835.8

* Isotope polymer molecular mass is calculated.

4.8 Chapter summary

Ab initio chain end funtionalisation via alkylation of silyl enol ethers in cationic polymerisation of isobutyl vinyl ether, ethyl vinyl ether and methyl vinyl ether were examined at different polymerisation temperatures applying tin tetrachloride as co-initiator. Highly functionalised oligomers were obtained when **SEE 1**, **SEE 2** and **SEE 3** were applied in the end-capping. It is considered that reactive silyl enol ethers can even cap the aldehyde and diisobutanol chain ends formed during polymerisation and increase the chain end functionality.

Side reactions in this polymerisation system were examined using the mass spectra and NMR spectra of the oligomer samples. *Ab initio* end-capping by reactive silyl enol ethers suppress the majority of side reactions during polymerisation; this was attributed to either the higher rate of end-capping than side reaction rates, or capping the formed side reaction chain end. Different silyl enol ether reactivities in end-capping were observed. The most reactive silyl enol ethers did not produce the highest chain end functionality.

Low polymerisation temperature was found to favour end-capping, probably because the low temperature helps to reduce side reactions. The best chain end functionality was obtained when **SEE 1** was applied in the polymerisation of EVE.

When **SEE 3** was applied, the system appeared to be better defined than with the control polymerisation without end-capping whilst the chain end functionalisation were also obtained. The conditions of performing kinetic research on end-capping were discussed.

From the experimental results, it is possible to set up a controlled cationic polymerisation system in which M_n, PD and chain end functionalisation can be regulated at the same time.

Chapter 5. Analysis of Oligo(vinyl ether)s with MALDI-TOF MS

5.1 Polymer analysis with MALDI-TOF MS

Matrix-assisted laser desorption ionisation time-of-flight mass spectrometry (MALDI-TOF MS) has been employed for analysing *ab initio* end-capping in cationic polymerisation of vinyl ethers. Well-resolved spectra of vinyl ether oligomers were obtained. The observed experimental oligomer masses agreed well with the theoretical values.

MALDI-TOF MS can give accurate absolute molecular weights of synthetic polymers as well as proteins. For polymer characterisation, the resolution of MALDI-TOF MS can be good enough to verify the polymer composition and structure of the polymer samples up to molecular weights of 15k Daltons. Within this range, MALDI-TOF MS is particularly applicable in the polymer chain end analysis. Different α-ends and ω-ends appear in MALDI-TOF mass spectra can be used to analyse the detailed polymerisation procedure, such as the mechanism of chain initiation, chain propagation, side reactions and chain termination. This led to further clarification of polymerisation mechanisms.

5.2 Sample preparation

It is regarded that sample preparation in a proper matrix plays a crucial role in the viability of the MALDI-TOF MS technique [Belu, 1996] for the characterisation of polymers. MALDI-TOF MS sample preparation is relatively easy for biomolecules because of their polar and water-soluble properties, which offers better interaction with water-soluble matrix and provides an effective site for ionisation. Sample preparation is especially difficult for non-aqueous, non-polar hydrocarbon polymers. Today many efforts are directed towards the development of highly reproducible sample preparation.

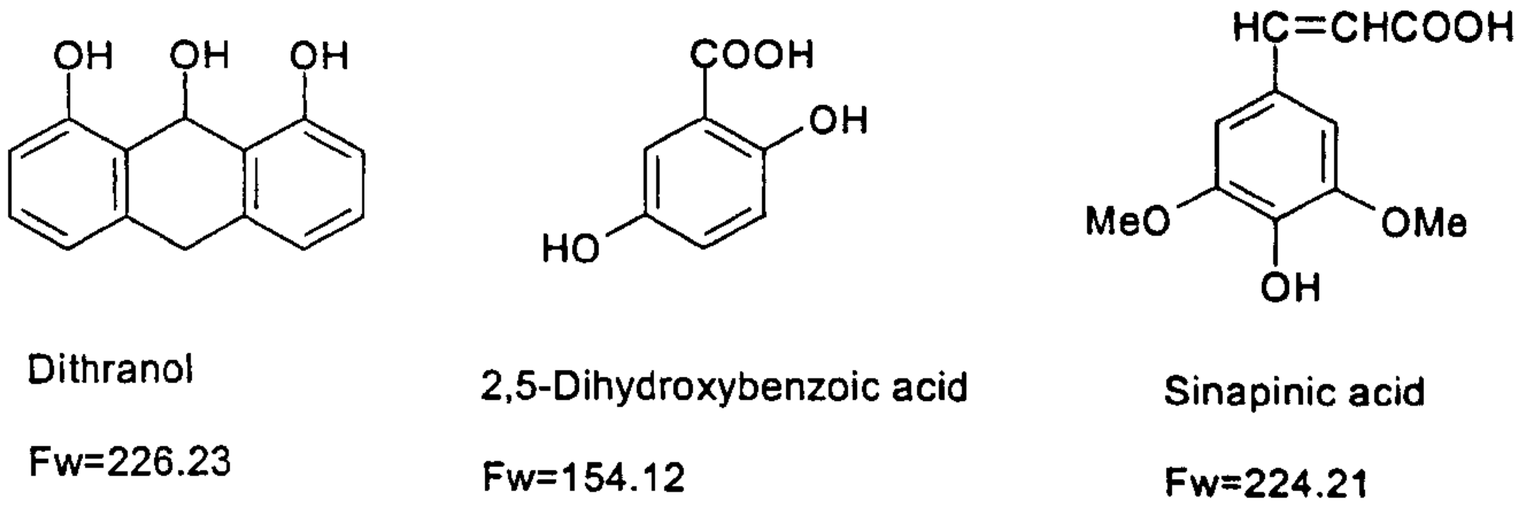
5.2.1 Application of matrices in sample preparation

The first polymer characterisation with MALDI-TOF MS performed by Tanaka et al. [Tanaka, 1988] who applied glycerol/polymer mixtures containing fine metallic particles as the laser-absorbing matrix. A poly(ethylene glycol) (PEG) with

polymer ion mass of 22k Daltons and a 4k Daltons of poly(propylene glycol) (PPG) were obtained. The ultra fine cobalt powder was applied to enhance the laser energy absorption.

Organic matrices were first applied by Karas, Bachmann and Hillenkamp to enhance laser desorption and ionisation of nonvolatile amino acids and peptides in 1985 using nicotinic acid as matrix [Wu, 1998; Karas, 1985]. In general organic compounds such as 1,8,9-trihydroxy anthracene (dithranol), 2,5-dihydroxybenzoic acid (DHB) and sinapinic acid, shown in figure 5-1, that contain aromatic and acid/alcohol sites were chosen for biomolecule MALDI-TOF MS analysis to enhance the absorption of laser energy, solubility and proton ionisation.

A standard method using sinapinic acid as a solid matrix was set up for the analysis of biomolecules in 1992. Danis first applied this sample preparation in analysing synthetic polymers [Danis, 1992]. They analysed polar water-soluble polymers like poly(acrylic acid) and poly(styrene sulfonic acid) which have good miscibility with sinapinic acid.



Dithranol

Fw=226.23

2,5-Dihydroxybenzoic acid

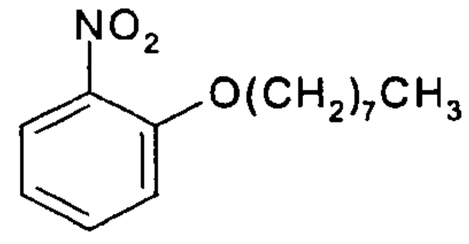
Fw=154.12

Sinapinic acid

Fw=224.21

Figure 5-1: Three organic matrices being applied in MALDI-TOF MS

The Hillenkamp group reported the applying of DHB as matrix in the analysis of PMMA, PEG and PPG in 1992. Alkali salts were applied to enhance the ionisation. They also demonstrated the analysis of hydrophobic polymer. MALDI-TOF mass spectra of polystyrene with molecular weight of 80k Daltons were obtained using liquid matrix of 2-nitrophenyl octyl ether (NPOE, shown in figure 5-2) together with AgTFA for cationisation.



NPOE Fw=251.33

Figure 5-2: 2-Nitrophenyl octyl ether

Danis and Karr [Danis, 1993] reported the development of the sample preparation by using organic soluble matrices to enhance the organic soluble polymer-matrix interactions in 1993. This organic solvent approach is very important for MALDI-TOF MS's polymer application because many of the polymers are non-water soluble and are non-polar. Danis and Karr's experiments showed the improvement of the applicable molecular weight, for example, PMMA was analysed with a molecular weight up to 260k Daltons; polystyrene with the molecular weight up to 120k Daltons. Polycarbonate, poly(vinyl acetate) and poly(vinyl chloride) were also analysed by this group.

The effect of matrix is to separate analyte molecules to reduce the intermolecular forces to facilitate the desorption of analyte molecules by strongly absorbing laser energy at the chosen range and to protect the analyte molecules from direct irradiation. Thus the matrix being applied should have strong absorption at the chosen laser wavelength; should minimally interfere with the mass spectrum; should not react with sample; should not contribute too much ions to the mass spectrum; should interact with the analyte to produce ions from ionic or neutral compounds and should effectively transfer energy to the ionised analyte to cause its release into vacuum. Also the matrix should be vacuum compatible. A considerably high matrix to analyte molecule concentration ratio is needed to prepare the target sample. Many strongly UV absorbing organic compounds were examined as potential matrices in MALDI-TOF MS analysis.

In the current analysis with MALDI-TOF MS, OiBVE samples with various relative polymer/matrix concentrations were prepared as shown in the following table 5-1. Different laser energy levels were applied to get the best spectra on each sample.

Table 5-1: Matrix and sample preparation in MALDI-TOF MS analysis

Matrix & concentration		OiBVE* concentration (mg/ml)		
		2	10	100
DHB (mg/ml)	2	+	+	+
	10	+	+	-
	100	-	++	++
Dithranol (mg/ml)	2	+	+	+
	10	-	-	++
	50	-	-	-

- OiBVE sample has a M_n of 1250, PD of 1.50

Generally lower concentration of polymer/matrix sample gives the better MALDI-TOF mass spectra. Too high matrix concentration like 100mg/ml, lead to the formation of big crystals and this retards the desorption of the analyte. However, high resolution MALDI-TOF mass spectra can be obtained when higher-level laser energy is applied.

The MALDI-TOF mass spectra of OiBVE with DHB as matrix have similar distribution of polymer ion series with the MALDI-TOF mass spectra of oligomer samples without the presence of matrix. When dithranol is applied as matrix, 2 extra main polymer series appear in the MALDI-TOF mass spectra.

Figure 5-3 compares the MALDI-TOF mass spectra of the same OiBVE samples prepared with different matrices. Figure 5-4 gives the expanded section of figure 5-3 containing two repeat units. It can be seen from figure 5-4 that oligomer series of 100n+14 and 100n+40 are not prominent when DHB is the matrix. And this is often observed even in the presence of ionisation agent.

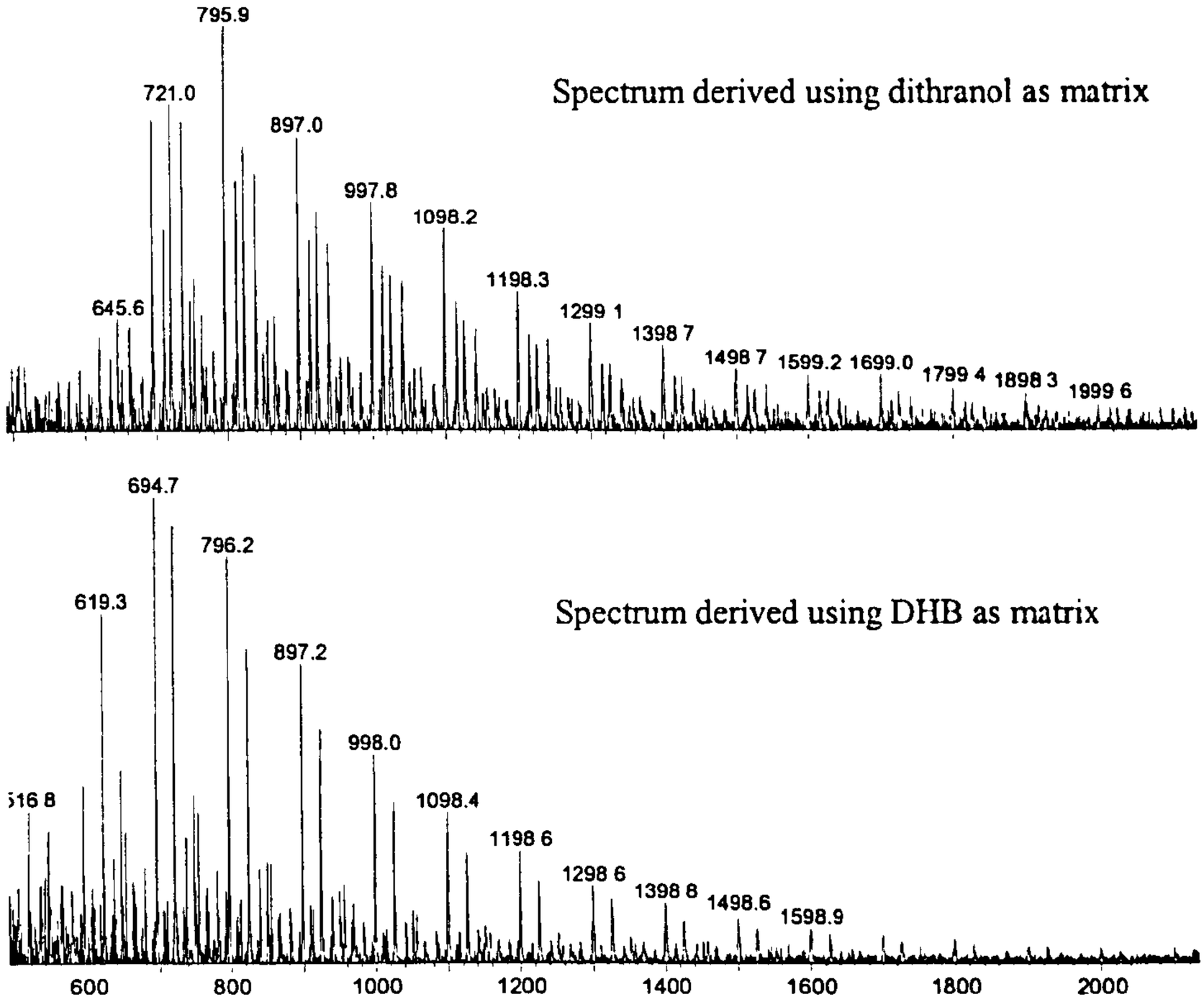


Figure 5-3: Application of various matrices in MALDI-TOF MS analysis

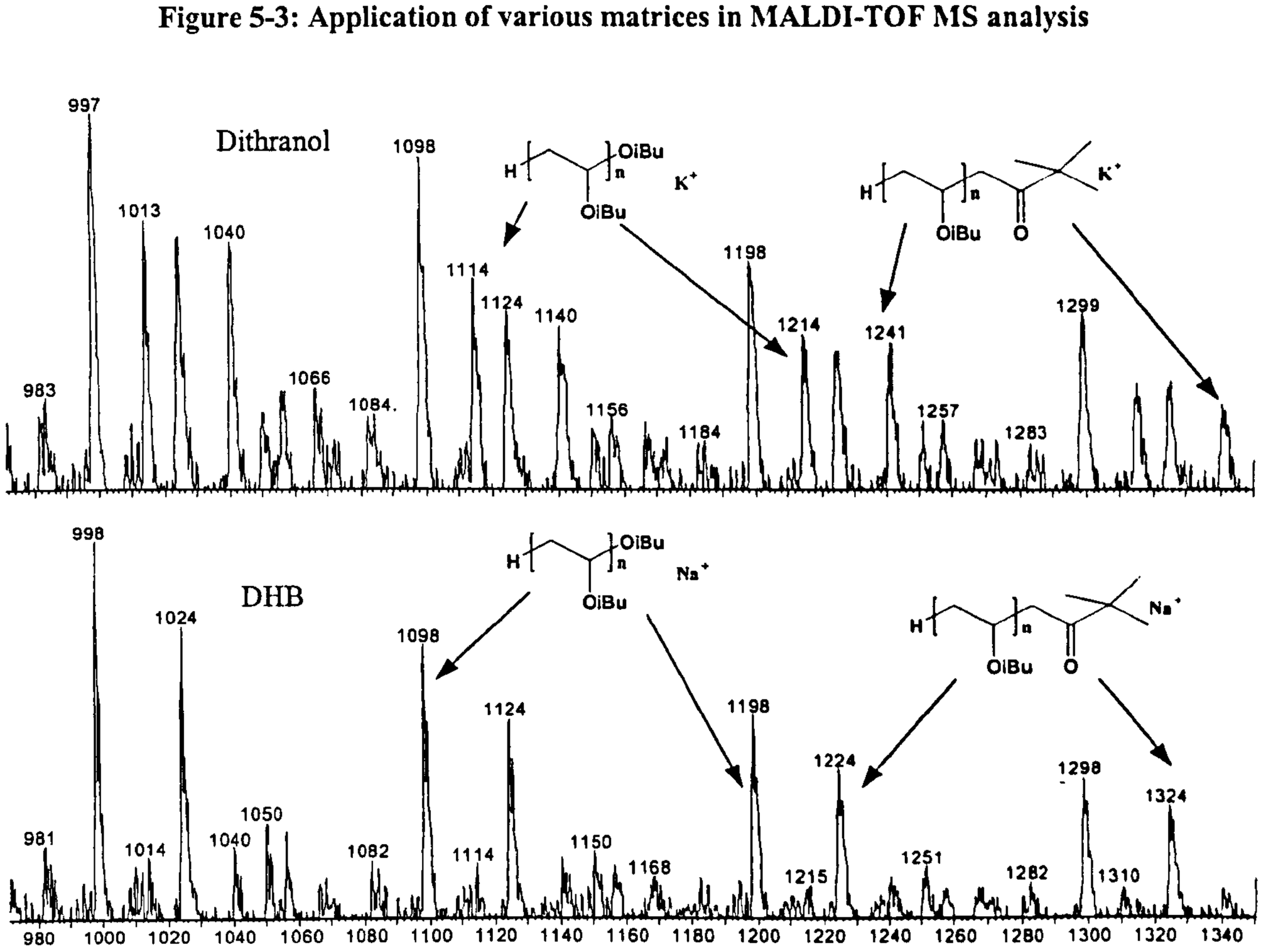


Figure 5-4: Expanded MALDI-TOF mass spectra of OiBVE samples with different matrices

When DHB is applied as the matrix the two prominent oligomer ion series are ketone functionalised chain end derived from alkylation of **SEE 3**, and diisobutanol chain end as labeled on figure 5-4. When dithranol is applied, however, the relative intensity of these two chain ends reduce and two new strong oligomer ion series appear. When we consider the attachment of potassium ion instead of sodium ion, these two new peaks can be explained well. Oligomer ions with the ion mass of 100n+40 are derived from the alkylation of silyl enol ether 3 by the functionalised chain end with potassium ionisation, while with the ion mass of 100n+14 is the OiBVE chain with diisobutanol chain end and potassium ionisation. The result indicates that compared with DHB, dithranol could enhance potassium ionisation. The conclusion can be further confirmed when a lower amount of dithranol is applied (iBVE/dithanrol=50:1), the potassium ionisation peaks are largely reduced. This enhanced potassium ionisation can also be observed when the potassium hydroxide aqueous solution instead of sodium hydroxide aqueous solution was applied in the oligomer recovery procedure following the polymerisation.

5.2.2 Direct laser desorption of OiBVE

MALDI-TOF mass spectra of OiBVE samples were obtained without the presence of matrix and ionisation agent, on both crude OiBVE samples and the fractional OiBVE samples from combination of a SEC and a fraction collector. The applicable OiBVE molecular weight is up to 2k Daltons. The oligomers appear to be ionised by sodium ions which probably come from the polymer recovery procedure, and also from contamination during the sample preparation procedure. This direct laser desorption generally requires a higher level of laser energy.

This observation is in accordance with the reports [Holm, 1987; Mattern, 1985; Belu, 1996]. Belu et al. got the MALDI-TOF mass spectra of polystyrene for molecular weights of 1k Daltons without matrix and ionisation agent. When ionisation agent is applied in sample preparation, MALDI-TOF mass spectra of polystyrene can be obtained on a molecular weight of 5k Daltons.

The crude oligomer samples (10mg/ml in THF) without any matrix and ionisation agent give MALDI-TOF mass spectra with sodium ionisation on oligomer ion series, but with higher noise level compared with those spectra with DHB as matrix. The fractional OiBVE samples (2.4mg/ml in THF) without matrix and ionisation agent give clear MALDI-TOF mass spectra with low noise level. Figure 5-

5 shows a MALDI-TOF mass spectrum of one of the SEC fractions of OiBVE end-capped by silyl enol ether 2. The prominent silyl enol ether 2 functionalised oligomer chains are clearly presented.

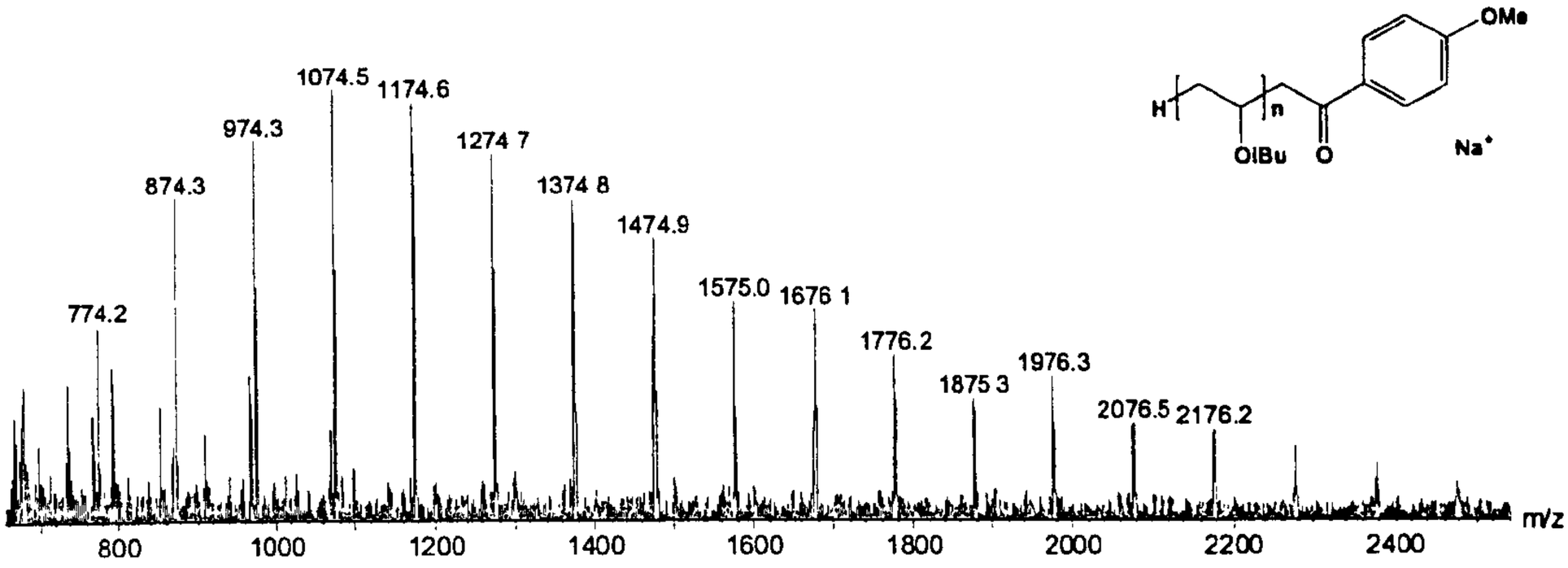


Figure 5-5: Direct laser desorption-time of flight mass spectrum of a fractionated OiBVE sample

It is not a rare observation that high resolution MALDI-TOF mass spectra of polymer samples were obtained without the presence of any matrix. From this direct laser desorption it seems that the desorption of OiBVE is not difficult. Also even at full laser energy level, apparent fragmentation of the oligomer chain was not observed.

The fractionated OiBVE samples have better resolved spectra and this could because of the lower sample concentration that reduced the analyte cluster thus favouring the desorption or sodium ionisation of the oligomers was enhanced during the fractionation procedure; or the fractionated sample has narrower molecular weight distribution than the crude sample.

5.2.3 Ionisation and the application of ionisation agents

In the current research ionisation agents were applied including NaI or silver trifluoroacetate (AgTFA). However, potassium ionisations were also observed. Table 5-2 summarises different ionisations being observed in MALDI-TOF mass spectra on 3 various chain ends.

Table 5-2: Different ionisation being observed in MALDI-TOF MS

Oligomer ion number	OiBVE ions with different ω-ends and ionisation	OiBVE ion mass* *m/z*	
		Theoretical	Experimental
1	H-(iBVE)$_{10}$-OiBu/Na$^+$	1098.0	1098.2
2	H-(iBVE)$_{10}$-OiBu /K$^+$	1114.1	1114.0
3	H-(iBVE)$_{10}$-OiBu / Ag$^+$	1181.9	1181.7
4	H-(iBVE)$_{10}$-CH$_2$-C(=O)-Ph/ Na$^+$	1243.9	1244.1
5	H-(iBVE)$_{10}$-CH$_2$-C(=O)-Ph/ K$^+$	1160.0	1160.3
6	H-(iBVE)$_{10}$-CH$_2$-C(=O)-Ph/ Ag$^+$	1227.9	1228.4
7	H-(iBVE)$_{10}$-CH$_2$-C(=O)-C(CH$_3$)$_3$/ Na$^+$	1124.0	1124.3
8	H-(iBVE)$_{10}$-CH$_2$-C(=O)-C(CH$_3$)$_3$/ K$^+$	1140.1	1140.0
9	H-(iBVE)$_9$-CH$_2$-C(=O)-C(CH$_3$)$_3$/ Ag$^+$	1107.8	1107.8

*: Monoisotope *m/z* values were applied

As mentioned above, washing the oligomer samples with potassium hydroxide aqueous solution instead of sodium hydroxide aqueous solution during the oligomer recovery procedure enhances the potassium ionisation in the MALDI-TOF mass spectrum as shown in figure 5-6 no matrix or ionisation agent was applied on this sample, the silyl enol ether 1 functionalised oligomer chains appeared to be ionised by sodium ion (with the oligomer ion mass of 100n+44) as well as potassium ion (with the oligomer ion mass of 100n+60). Another series that appear on the spectrum are the oligomer chain with diisobutanol chain ends and potassium ionisation (with the oligomer ion mass of 100n+14). This seems to indicate that compared with sodium ionisation potassium ionisation favours diisobutanol chain end.

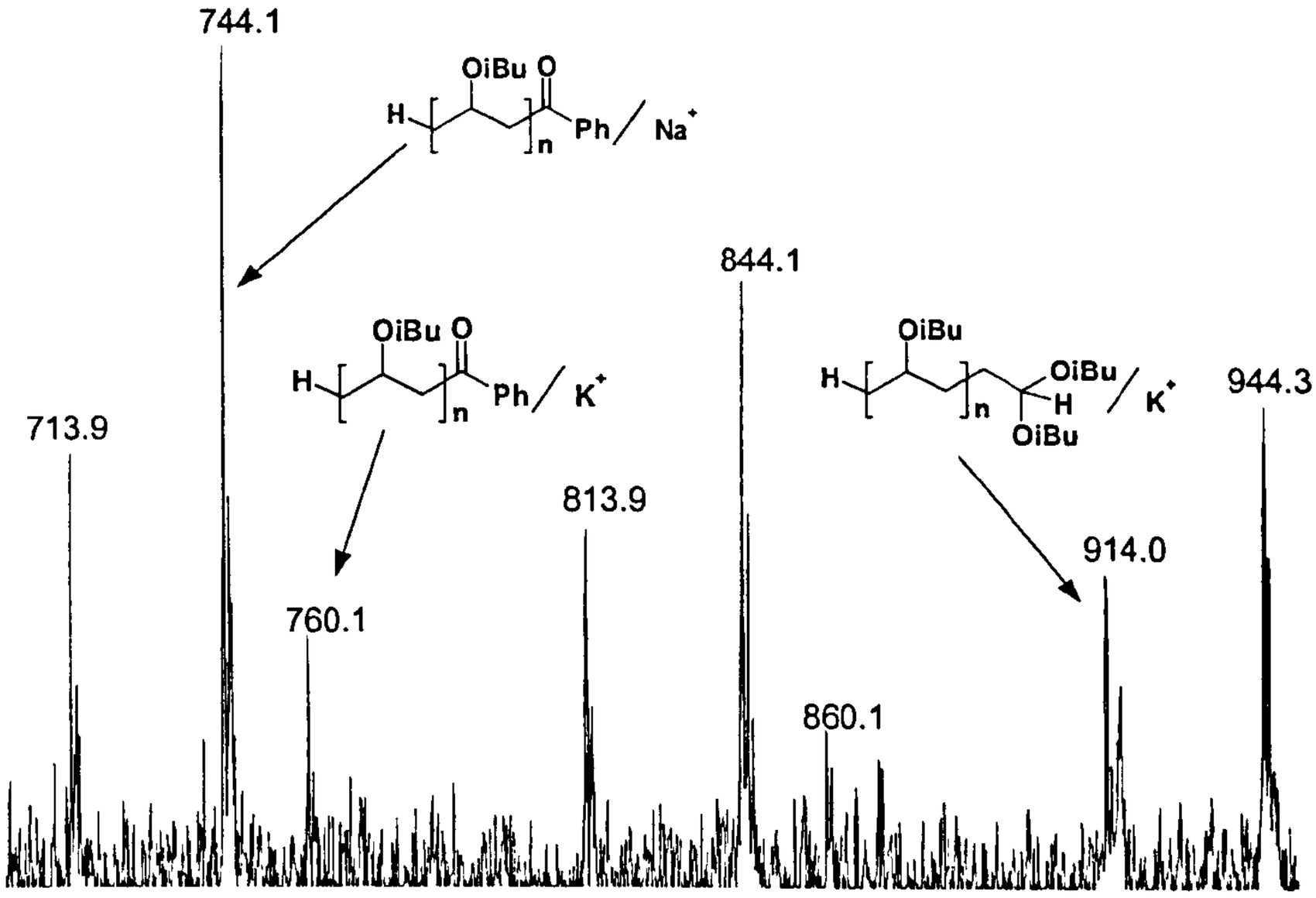


Figure 5-6: The enhancement of potassium ionisation

When AgTFA is applied as a ionisation agent, it is observed that the relative intensity of oligomer chains with different ω-end changed. Figure 5-7 shows the MALDI-TOF mass spectra of the same OiBVE sample prepared under the same conditions, except that the upper spectrum in the figure is obtained with AgTFA as ionisation agent and the lower spectrum is obtained with the absence of any ionisation agent. Again an expanded spectrum is shown below as figure 5-8.

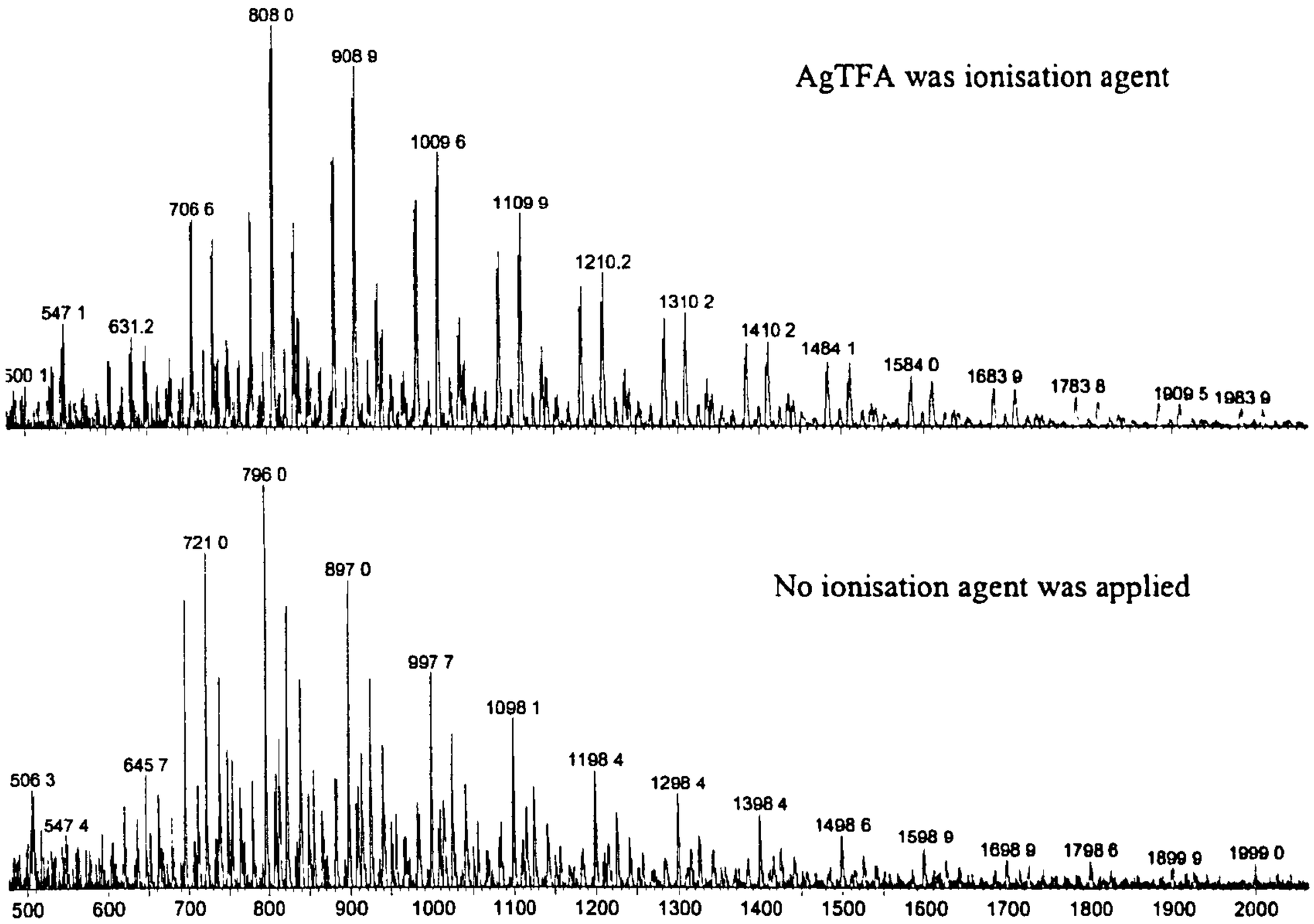


Figure 5-7: The application of AgTFA as ionisation agent in MALDI-TOF MS

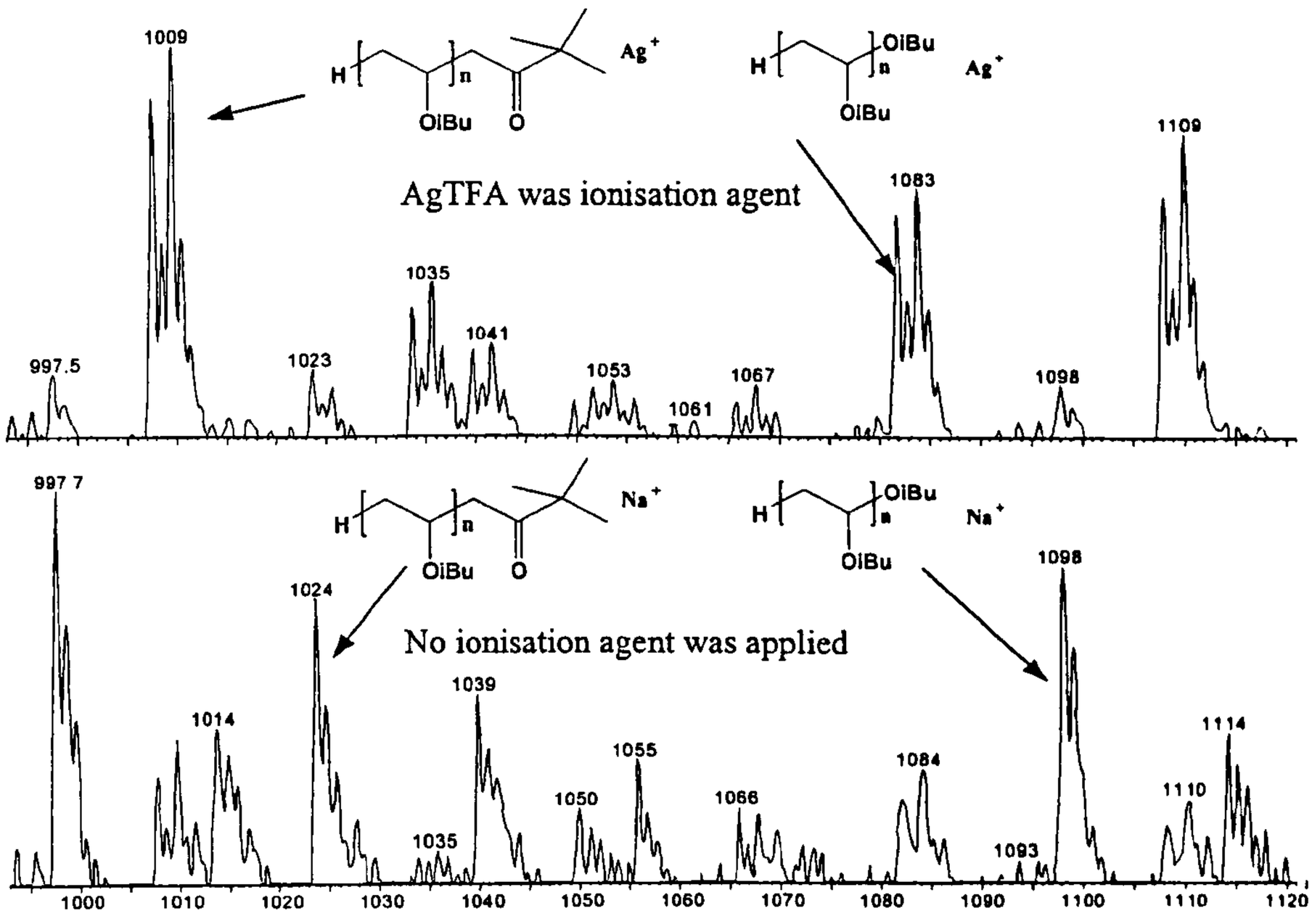


Figure 5-8: Expanded MALDI-TOF mass spectra of figure 5-7, the apply of AgTFA as ionisation agent

From figure 5-7 and figure 5-8 it can be seen that oligomer ion series of silyl enol ether 3 functionalised chain end with silver ionisation (with the ion mass of 100n+8) shows higher intensity than silver-ionised diisobutanol chain end (with the ion mass of 100n+82). Sodium ionisation shows different relative intensity of these two oligomer ions. The difference between these two oligomer chains only lie in the different structure of the chain end, these contrary relative intensities indicate that silver ion could be more liable at the polymer chain end and that ketone chain end pick up silver ion more easily than does the diisobutanol chain end.

It is reported that silver cationation is facilitated by polymers containing unsaturated bonds [Belu, 1996]. The same report indicates that non-polar polystyrene is more likely to be cationised by silver salt than alkali metal salt. This is regarded to be due to the affinity of Ag^+ for the benzene ring. The size of the benzene ring and its electron-rich properties is suitable for carrying silver ion. Due to the observation of the attachment of silver ion to poly(methyl mathacrylate) (PMMA) but not poly(ethylene oxide) (PEO), Belu suggested that Ag^+ may form adducts with ester functionality instead of saturated polymers containing oxygen moieties. According to our observation, Ag^+ could form adducts with ketone instead of ester functionality.

Attention was also paid to the special shape of mass peaks with silver ionisation. Unlike ionisation with Na^+, K^+ and H^+, in which the monoisotope mass of the oligomer ion turned out to be the strongest at the low molecular weight range, the silver ionisation showed two strong peaks due to the comparable relative abundance of silver isotopes[a]. These special double peaks can be used to diagnose silver ionisation as shown in figure 5-9.

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[a] Atomic weight of silver is 106.90509, relative abundance 51.85%, atomic weight of silver isotope is 108.90470 with the relative abundance of 48.15%

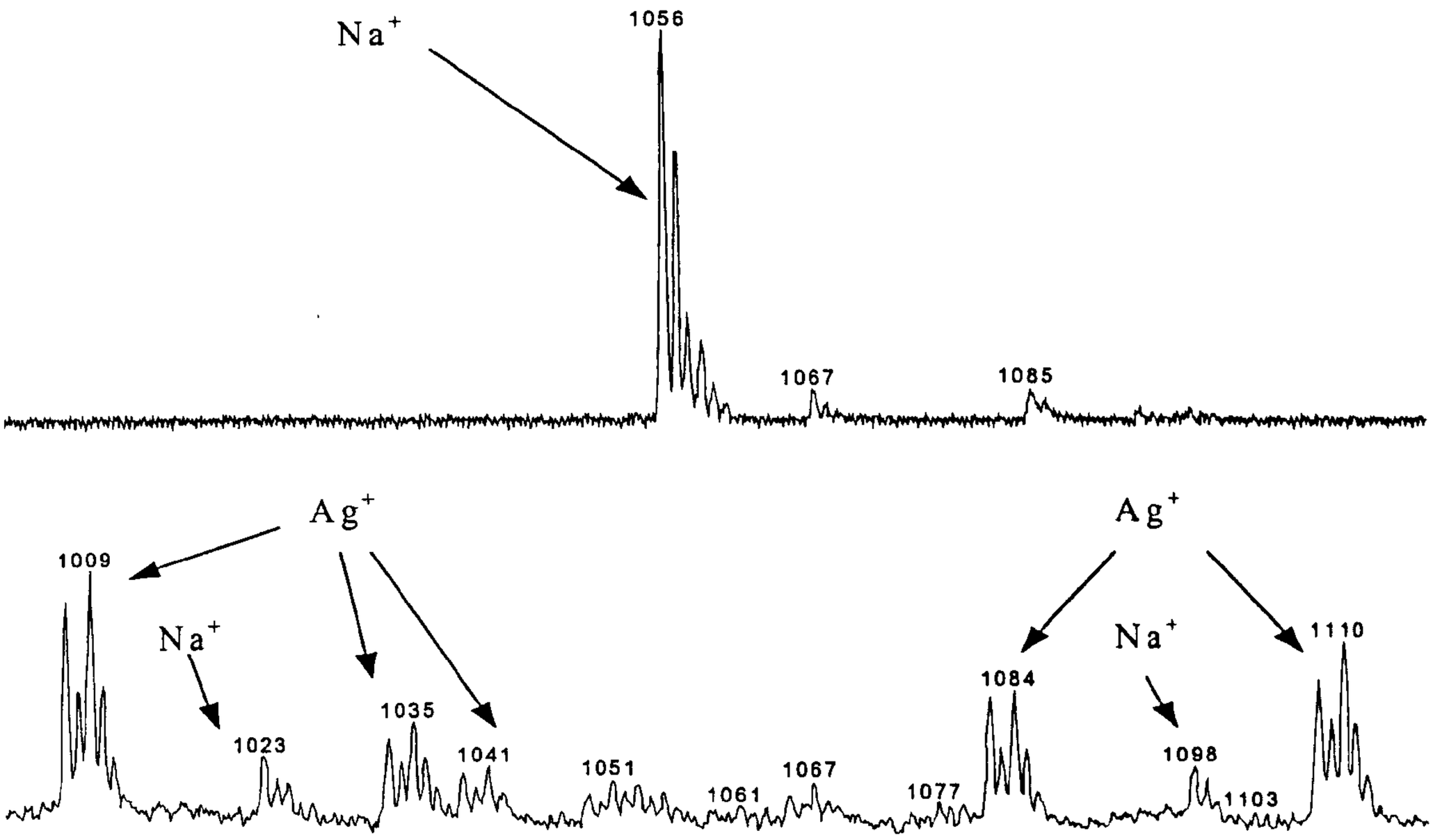


Figure 5-9: Diagnose of silver ionisation in MALDI-TOF mass spectrum

When NaI is applied in the OiBVE sample preparation, the noise level is generally decreased compared to the spectrum without ionisation agent. This is what we expected. Unlike PMMA and PEO, OiBVE is a less polar polymer, but in the presence of the heteroatom (oxygen), OiBVE seems to pick up sodium ion easily. Even when without the presence of sodium salt as ionisation agent and without matrix, OiBVE shows prominent sodium ionised oligomer chains.

5.3 Combination of SEC and MALDI-TOF MS

It is reported that MALDI-TOF MS can not give reliable molecular weight information for polymers with broad molecular weight distribution [Schriemer, 1997; Wu, 1998]. The combination of SEC and MALDI-TOF MS [Simonsick, 1993] offers a method to provide polymer samples with very narrow molecular weight distribution to obtain reliable polymer molecular weight parameters.

In practice, the SEC fractions of the polymer sample were collected and MALDI-TOF MS analysis was applied to each fraction. The average molecular weight of each fraction was then determined according to the resultant MALDI-TOF mass spectrum. Combined with the relative intensity of each fraction determined by

SEC, the more reliable absolute oligomer molecular weight could be obtained. The average molecular weight of each fraction can also be used to calibrate the SEC column. The calibrated column and the SEC trace can be used to determine molecular weight information of unfractionated polymer samples [Montaudo, 1995a; Danis, 1996b]. This calibration avoids the error due to the polymer structure differences between the calibration standard and the polymer samples. It is especially applicable when SEC standards are not available for calibration.

To combine the SEC and MALDI technique, a fraction collector was connected to the SEC column. SEC fractions were collected from elution time of 18 to 30 minutes. 12 fractions were collected for each OiBVE sample, each fraction contains one minute of eluent. The collected SEC fractions were analysed by MALDI-TOF MS as shown in figure 5-10.

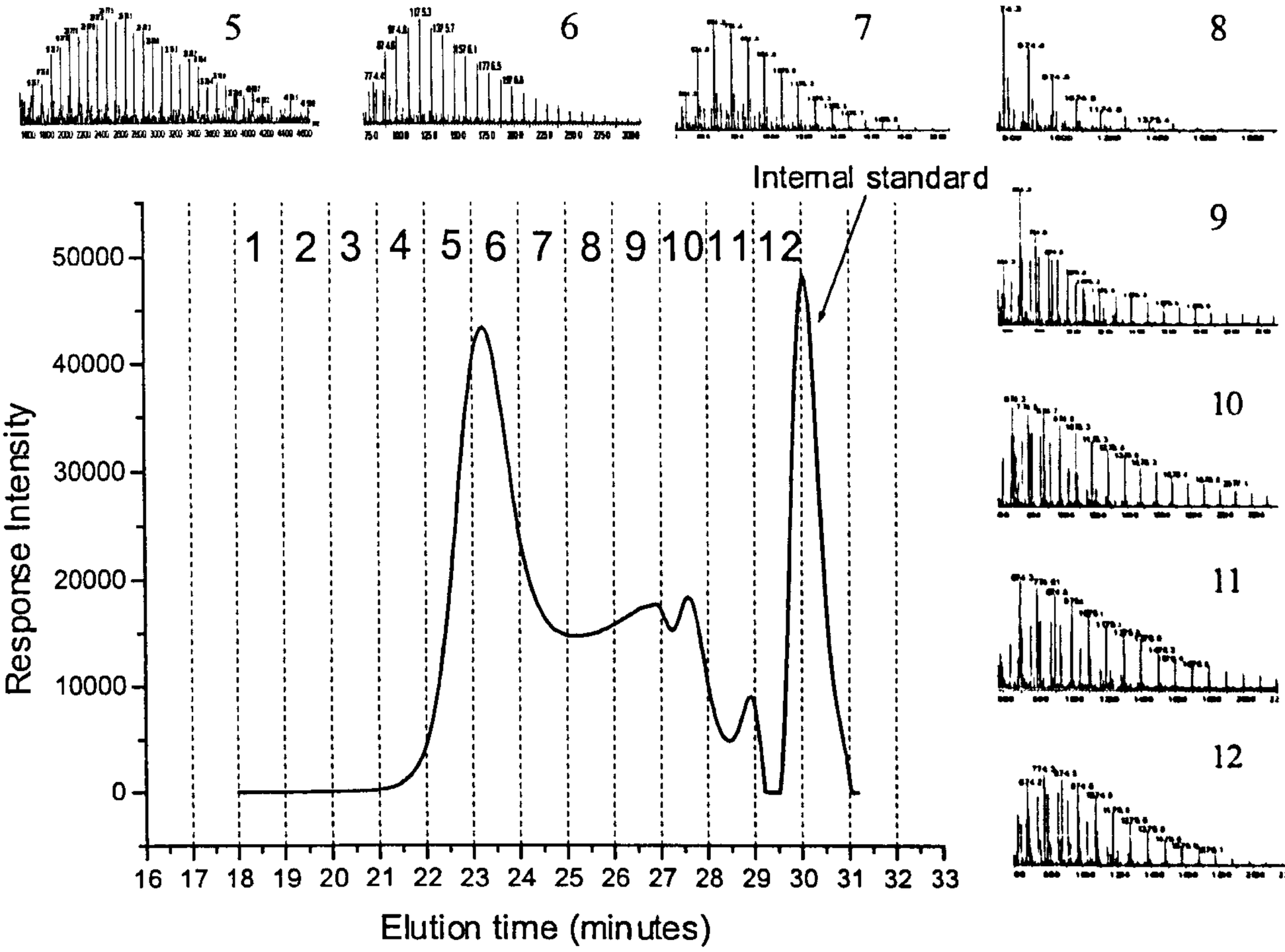


Figure 5-10: Combination of SEC and MALDI-TOF MS

It can be seen from figure 5-10 that the SEC and MALDI-TOF MS analysis are accordance with each other, that MALDI-TOF mass spectra were obtained since the No. 5 fraction and that this sample has more Gaussian molecular weight

distribution whilst the rest of the fractions have more tailed molecular weight distributions. Also the molecular weight of the following SEC fractions shift to a lower value and have more tailed molecular weight distribution.

The average molecular weight of each SEC fraction was calculated manually according to MALDI-TOF mass spectral data. Figure 5-11 shows the plot of average M_n to SEC elution time. Each M_n is calculated from respective MALDI-TOF mass spectrum. These data can be used to calibrate the SEC column and calculate molecular weight and molecular weight distribution.

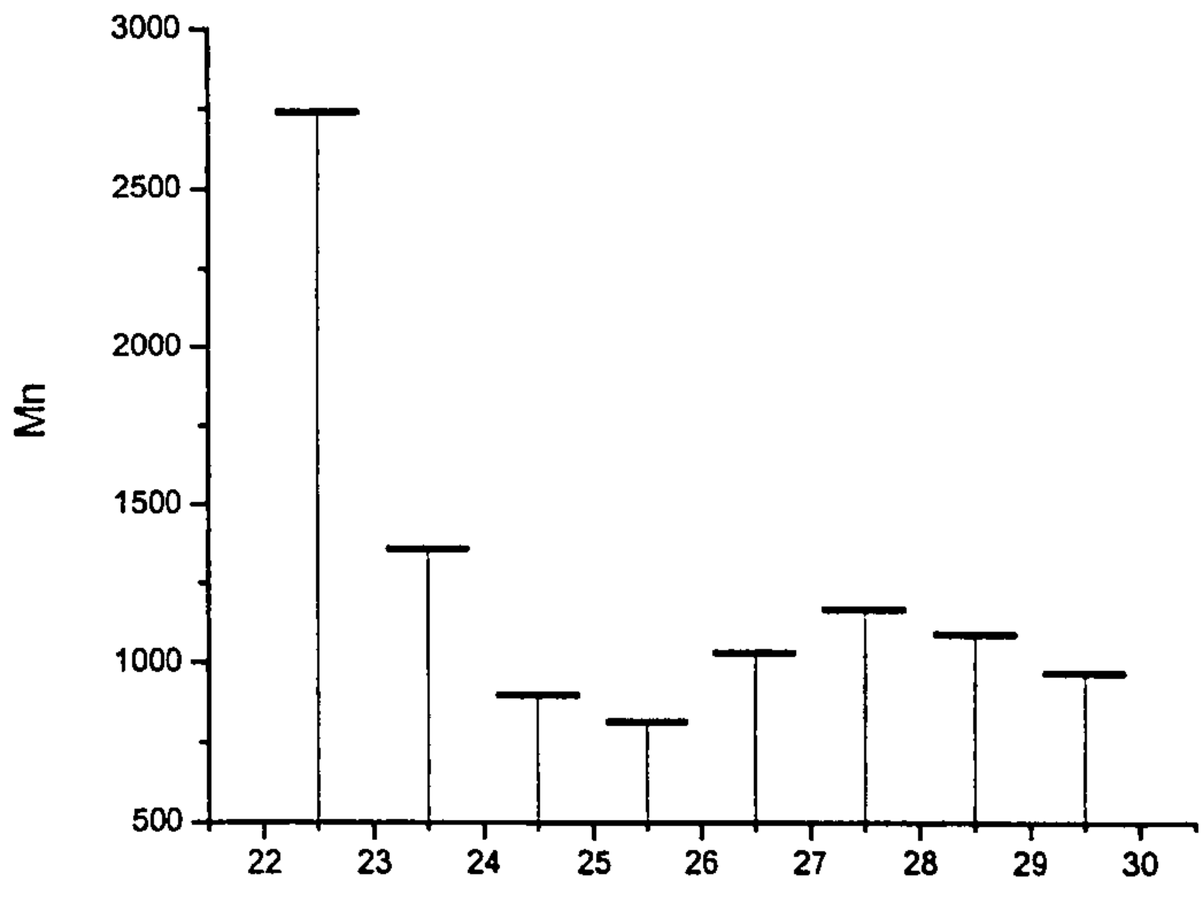


Figure 5-11: Calibration of SEC column by the combination of SEC-MALDI

5.4 Can MALDI-TOF MS analysis be quantitative?

5.4.1 Quantitative chain end functionality analysis

Can MALDI-TOF MS be quantitative in analysing chain end functionality in the current research?

Polymer ion intensity can be influenced by polymer desorption probability, extent of fragmentation and ionisation, detection probabilities etc. For polymers with low molecular weights of 1k and narrow polydispersities of lower than 1.10. These influences can be assumed to be constant, but with the determining of chain end functionality, application of MALDI-TOF MS becomes more complicated by the presence of different end-groups. The end-groups could affect the ionisation and

eventually affect the relative intensity of polymer ions carrying them. This effect could be caused by many reasons, like the ability of the chain end to take an ion, or even surface energy of the end group. The effect of end-groups on polymer ionisation should be stronger for shorter polymer chains. However, Belu and co-worker's research on the relative ion yield of polystyrene carrying different chain ends gave an overall chain end ratio close to the actual value even at the low molecular weight of 1.5k Daltons. The result indicates that the effect of end-group on ion yield is not significant.

A research report [Nontaka, 2001] also indicates the phenomena of laser-induced halogen loss. This could be the reason that the chlorine chain end has never being observed in our MALDI-TOF MS analysis. Various chain ends appeared in the current end-capping research mainly including alkoxy chain end, diisobutanol chain end, ketone chain end and ester chain end. We discussed in the above sections that the presence of phenyl and ketone sites cause the affinity for Ag ion, but not sodium ion. Sodium ion is more probable to attach to a polymer chain containing heteroatoms like oxygen. So that the sodium ionisation efficiency should be identical to polymer chains with similar heteroatom moieties and the ionisation yield difference caused by different chain ends is assumed to be low. Thus chain end functionalities can be compared according to MALDI-TOF mass spectra.

Figure 5-12 is the comparison of the chain end functionalities of two OiBVE samples obtained from their ^{1}H NMR spectra and MALDI-TOF mass spectra respectively. The squares in the figure give the chain end functionalities obtained from subtracted MALDI spectra by comparing different chain end intensities within one repeat unit. The filled points show data from OiBVE sample polymerised at -78°C, while for the open squares give the chain end functionalities of OiBVE polymerised at -15°C. NMR analysis gave the average chain end functionality, for OiBVE prepared at –15 and -78°C sample, as 70% and 86% respectively.

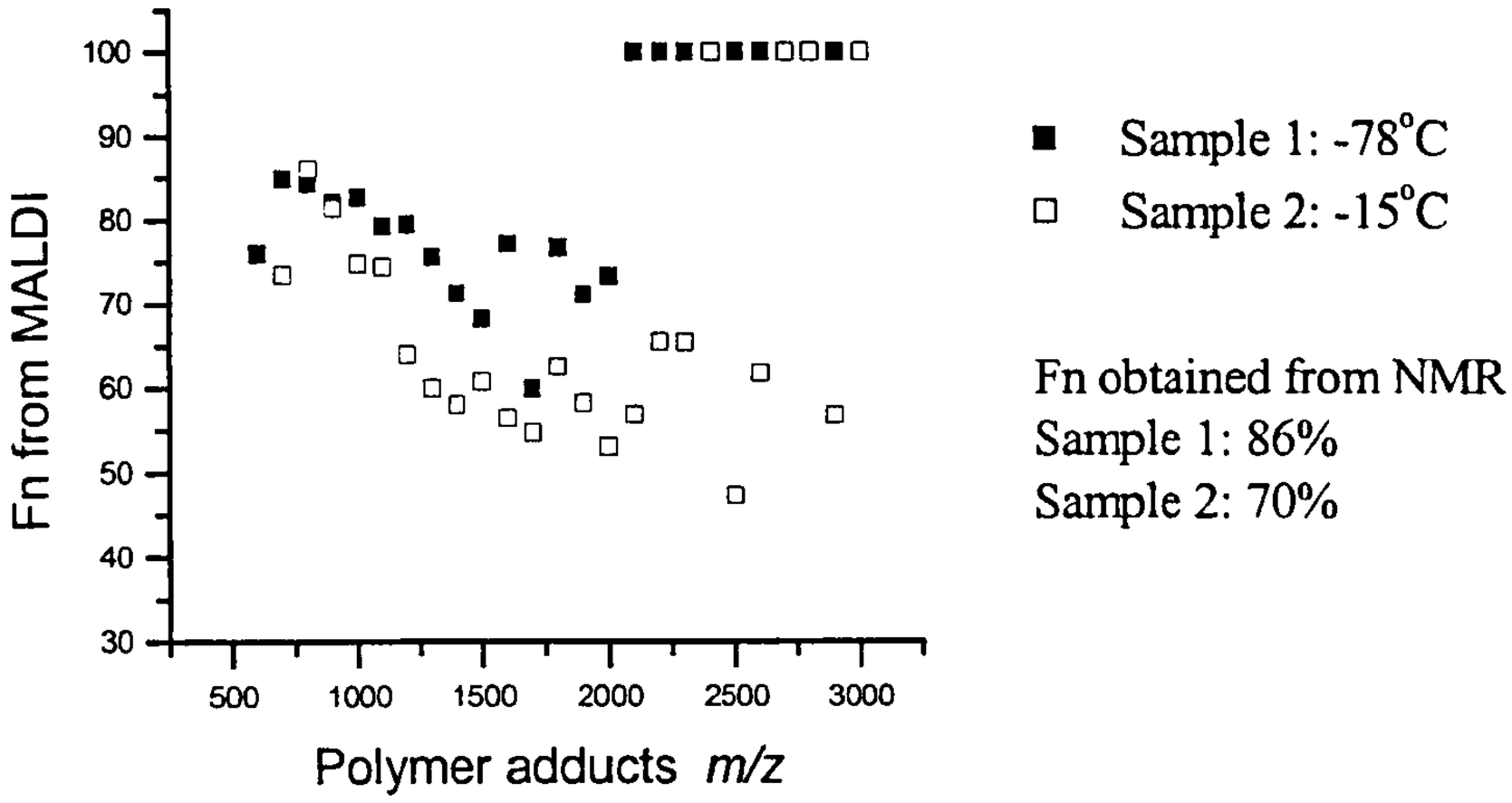


Figure 5-12: Comparison of chain end functionalities obtained from MALDI-TOF MS and NMR

However the data in figure 5-12 essentially agree with the average functionalities obtained from the NMR spectra of the two samples and comparison over the small mass ranges used when comparing oligomers of constant repeat number appears to be a valid procedure.

The NMR method for determining the fraction of chains with the desired functionality is also associated with errors. For example the precision in chain end functionality values depend on signal to noise ratio, which can be low when attempting to integrate end groups at low concentration. Furthermore, the overlapping of the α-end ^{1}H resonance and ω-end ^{1}H resonance makes it impossible to detect chain end functionalities quantitatively according to NMR analysis.

5.4.2 Molecular weight distribution from MALDI-TOF MS

As mentioned previously, the MALDI-TOF process suffers from problems associated with heterogeneous sample preparation, uneven polymer ion desorption and possibly uneven ionisation. Although new techniques like electrospray sample deposition for preparing MALDI-TOF MS samples that provides uniform surface-analyte distribution and increases the reliability of quantitative analysis [Hensel, 1997]. Belu et al. [Belu, 1996] explored the accuracy of M_n obtained by MALDI-TOF MS and SEC by measuring the shift of M_n of the polystyrene with different terminating groups. All of their polystyrene samples have the polydispersity of lower than 1.1. Under this condition, the shift of M_n observed by MS method is only 6%

different from the expected value, more accurate than the SEC value, which is 16% in error. Their conclusion is: the molecular weight distribution obtained by MS is more informative than SEC in a mass range of below 10k Daltons. Other former experiences on quantitative application of MALDI-TOF MS techniques indicate that with narrower PD polymer samples within certain mass range, together with the right matrix and sample preparation, MALDI-TOF MS can be quantitative in determining molecular weight and molecular weight distribution information. For example, it is reported that MALDI-TOF MS produces the right molecular weight information in polymer samples with narrow molecular weight distribution of PD<1.2 [Montaudo, 1995b].

SEC expresses all-size polymer chains as a relative value. MALDI-TOF MS expresses the accurate absolute values of polymer ions. If the molecular weight distribution obtained from MALDI-TOF MS is accordance with the molecular weight distribution obtained from SEC, then MALDI-TOF MS's expression of the polymer's molecular weight distribution is more reliable. Figure 5-13 shows the comparison of molecular weight distribution from SEC with the MALDI-TOF mass spectrum of the same sample.

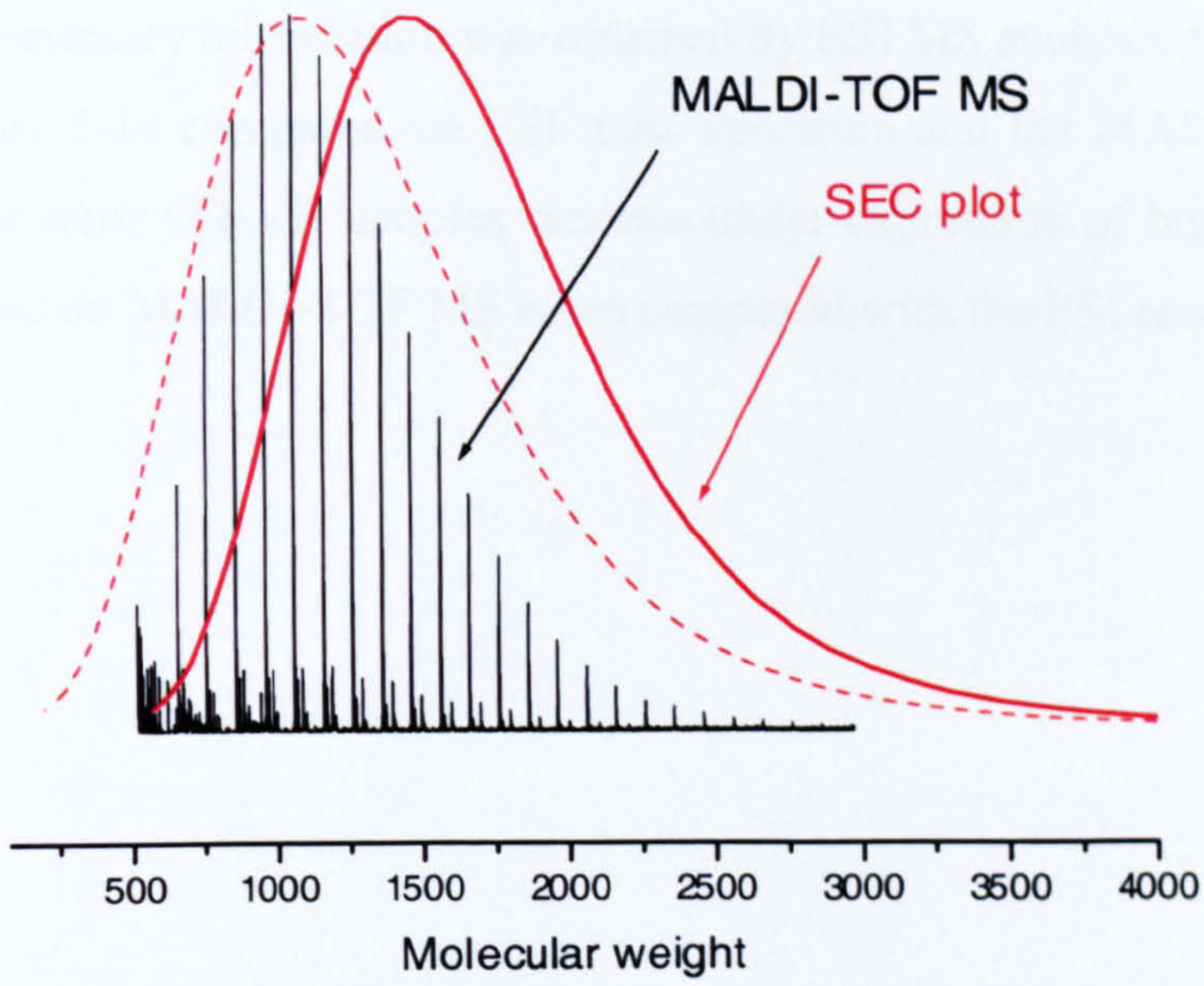


Figure 5-13: Molecular weight distribution from MALDI-TOF MS and SEC

[iBVE]:[iBVE-HCl]:[SnCl4]:[*n*-Bu4NCl]=10:1:1:0.5:0.75, initial [iBVE]=0.38 mol L^{-1} Polymerisation time: 5minutes, polymerisation temperature: -78°C, M_n=1370, PD=1.10

In figure 5-13, apart from MALDI-TOF mass peaks of oligo(isobutyl vinyl ether), the red solid line is the SEC plot of molecular weights versus the responses. Considering the fact that SEC gives relative molecular weight value based on calibration, it is not surprising to observe that the molecular weight distributions from SEC and MALDI-TOF MS are not perfectly in accordance.

The red dashed line in figure 5-13 is the shifted SEC plot, for easy comparison of the molecular weight distribution from both analysis methods. The shifted red dash line can not be totally accordant with the MALDI-TOF mass spectrum and shows slight mass discrimination at higher molecular weight range of the MALDI-TOF MS. Although SEC only gives a relative value of molecular weight, the weight fraction information it provides is accurate. This comparison only indicates that a MALDI-TOF mass spectrum could not give the perfectly accurate information on molecular weight distribution of the oligomer even when the sample has a narrow PD. The observed mass discrimination could be caused by sample preparation, mass-dependent desorption/ionisation processes and/or mass-dependent detection efficiency [Wu, 1998].

5.5 Comparison of MALDI-TOF MS and ESI-MS

Complementary information was obtained by ESI MS analysis of the oligomer samples. Figure 5-14 compares the ESI mass spectrum and the MALDI-TOF mass spectrum of the same OiBVE samples. Serious under-expression of higher molecular mass is observed on MALDI-TOF MS when compared with the ESI result.

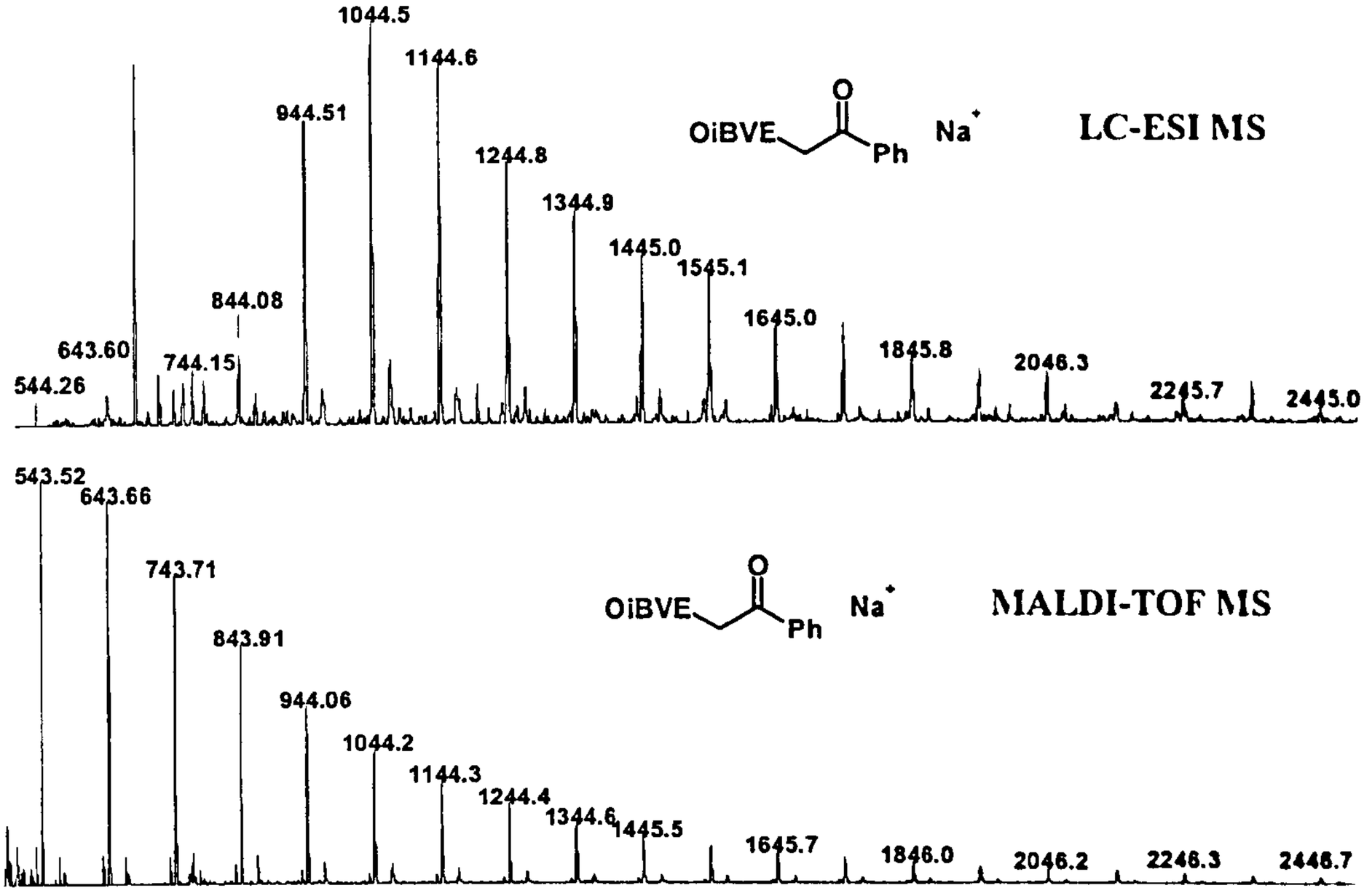


Figure 5-14: Comparison of ESI MS and MALDI-TOF MS on OiBVE sample

The ESI mass spectrum confirmed the high chain end functionality of the oligomer sample. Both MALDI and ESI show that the dominant chain end arises due to alkylation of silyl enol ether 1 by the propagating chain end and the repeat unit of m/z = 100, for OiBVE, is clearly seen. In both spectra these is little evidence for methoxy chain ends. However, it can be seen that the MALDI process was subject to under-presentation of oligomer chains with higher molecular weight so that the distribution of oligomer ions were shifted to lower molecular weight. According to the MALDI-TOF mass spectrum, the oligomer chain with 3 repeat units (m/z = 543.5) had the highest intensity and this indicates that many very short functionalised oligomer chains were formed. On the other hand the ESI result showed that the same oligomer chain (m/z = 544.2) was less than 10% of the intensity of oligomer chain with 9 repeat units. Considering the initial monomer to initiator to silyl enol ether ratio of 10:1:1, it can be assumed that end-capping reaction occourred when monomer was largely consumed. The polymer ion distribution of ESI is more reliable than MALDI due to the different sample introduction procedure. ESI avoids the difficulties that non-homogeneous sample preparation, and uneven polymer ion desorption that MALDI can introduce. However, multiple charging was sometimes observed in the

ESI analysis, although this was not seen in the sample shown in figure 5-14.

If the ion yield and the oligomer distribution are both reliable, then the very high chain end functionality conclusion is also reliable. NMR shows the chain end functionality of this sample is 86%. By cross-checking with MALDI-TOF MS, ESI MS and NMR, the oligomer chain end functionality is proved to be high.

The relative intensities of the various mass peaks derived from the ESI process were similar to those derived from MALDI-TOF MS. Therefore, it is reasonable to assume that the different chain end structures do not seriously affect sodium ionisation to OiBVE and that the ionisation site does not mainly lie on chain end. The ESI result indicated that not many oligomer chains with repeat numbers less than 7 were formed during the *ab initio* end capping. This is an important observation since very low molecular weight oligomers could cause problems in some applications, for example if they were to leach from the final material. The above experiments indicate that the MALDI process can not be used to produce accurate molecular weight distributions.

MALDI-TOF MS is an extremely sensitive technique and gives predominantly singly charged ions. Figure 5-15 compares MALDI-TOF mass spectrum (the top one) of an OMVE sample with its ESI mass spectrum (the bottom one). Again, the prominent oligomer ion series on both spectra are OMVE with the same α and ω-end as well as sodium ionisation. The bottom ESI mass spectrum shows multiple charge between 1.0k Daltons to 1.4k Daltons, including double and triple charging. Generally longer polymer chains carry more than one charge. Detailed scrutiny over the spectrum found that the double charge over the range of 1.0k Daltons to 1.4k Daltons is due to the attachment of two sodium ions. The mass spectra with double and/or triple charged oligomer ion will affect the overall appearance of molecular weight distribution of the polymer and complicate the chain end functionality analysis. In the current MALDI-TOF MS analysis the multiple charge has never been observed.

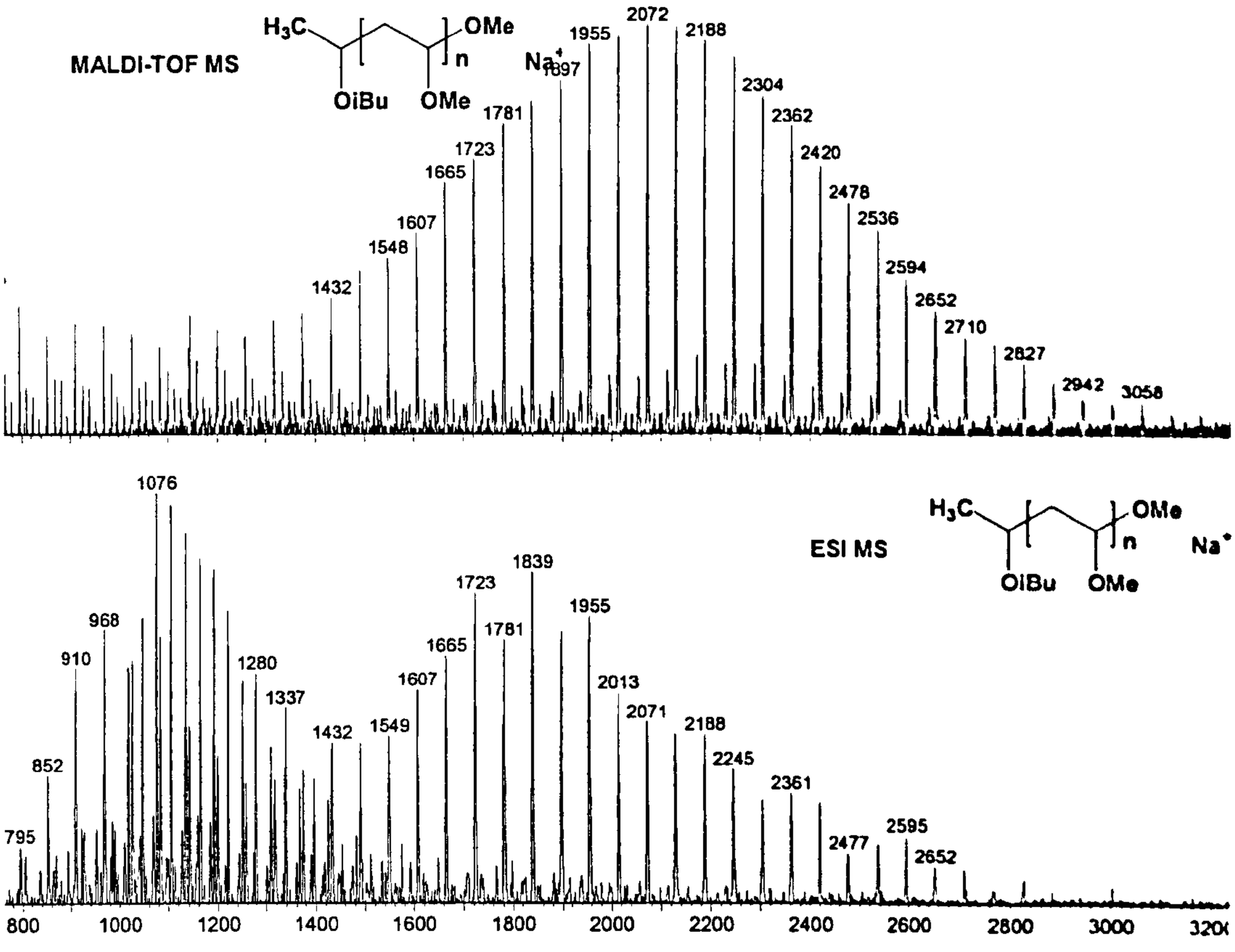


Figure 5-15: Compare of MALDI-TOF MS and ESI-MS on OMVE sample at a higher molecular weight

It can be seen that each technique has its advantages and drawbacks. Complementary information is required to get clear view during analysis.

5.6 Chapter summary

While NMR and IR sometimes offer the structure—dependent information on polymer samples, accurate compositional information can be obtained by the structure—independent mass spectra of synthetic polymers that can be used to analyse end group and structure of polymer chain.

MALDI-TOF mass spectra provide accurate mass information, quick and easy analysis. It is a more qualitative technique for giving the information on structure characterisation. It could not yet provide accurate quantitative information on M_n, M_w or the polymer distribution, especially for polymer samples with broad molecular weight distribution.

Although mass discrimination effects exist, the different chain end intensity can be compared within a certain mass range—assume that the polymer chain is long enough that the different chain end structure doesn't affect the molecule's desorption and ionisation, so that accurate chain end functionality can be obtained in a range of polymer ion mass. Because of the underpresentation of high-mass polymer, doubts still exist in calculating the average chain end functionalities of the polymer samples. But when other accurate measurement is not available MALDI-TOF MS can be used for the estimation of chain end functionality.

Because of the good resolution of this technique, accurate polymer mass (errors fall within 0.4 Dalton for the polymer ion mass of around 1k Daltons) can be obtained to detect the different polymer chain end structures formed during polymerisation and thus analyse the side reactions.

MALDI-TOF mass spectra are not proved to be reliable on quantitative analysis on molecular weight information due to two reasons, i.e., polymer ion desorption is selective in that shorter polymer chains are easier to desorb than longer polymer chains and solid polymer samples are not homogeneous and produce non-comprehensive polymer ion expression. Under the condition of comprehensive expression of the sample, and within 20 Daltons' mass range, the relative intensity of the signals could be compared quantitatively if different ionisation effects due to different chain end structures are negligible, and the chain end functionality could be obtained this way. The relative intensity obtained at different polymerisation conditions can be used to illustrate the detailed cationic process.

Chapter 6. Conclusions and Future Work

6.1 Conclusions

Cationic polymerisation of isobutyl vinyl ether, ethyl vinyl ether and methyl vinyl ether were performed using different initiation systems and under various polymerisation conditions. *Ab initio* chain end functionalisations via alkylation of silyl enol ethers in cationic polymerisation of vinyl ethers were explored. MALDI-TOF mass spectrometry was applied to analyse the obtained oligo(vinyl ether)s so that the polymerisation process and chain end functionality can be better revealed.

6.1.1 Cationic polymerisation of vinyl ethers

Cationic polymerisation of isobutyl vinyl ether was performed with various binary initiation systems including: iBVE-HCl/$Yb(OTf)_3$; iBVE-HCl/$SnCl_4$; iBVE-HCl/$SnBr_4$; HCl/$ZnCl_2$ and EDGE-$(HCl)_2$/$Yb(OTf)_3$.

Yb(OTf)3 is reported as a potential water tolerant Lewis acid [Satoh, 1997]. With potential application in emulsion cationic polymerisation in mind this Lewis acid was first investigated in the cationic polymerisation of isobutyl vinyl ether. In our conditions, polymerisations that were catalysed by $Yb(OTf)_3$ gave oligomer samples with broad molecular weight distributions. The lack of further chain growth and the presence of aldehyde and alkene chain ends observed from NMR indicated a non-living polymerisation system. The results are in accordance with the former report [Satoh, 1997]. The aldehyde chain ends probably come from the intramolecular termination of the propagating chain-end via elimination of 2-methylpropene and/or water capping of the carbocationic chain end. The analysis of the polymerisation process showed that lower $Yb(OTf)_3$ concentration led to slower polymerisation and higher molecular weight as expected.

The iBVE-HCl/$SnCl_4$ initiation system gave oligo(isobutyl vinyl ether)s with narrower molecular weight distributions than the iBVE-HCl/$Yb(OTf)_3$ initiation system, especially at -78° and in the presence of *n*-Bu_4NCl the polymerisation was shown to be a controlled cationic polymerisation. However, at raised polymerisation temperatures and/or in the absence of added nucleophile side reactions are still observed.

Side reactions in this polymerisation system were examined using mass spectra and NMR spectra of the oligomer samples. Under less critical polymerisation conditions 7 different chain ends from side reactions are observed in MALDI-TOF mass spectra. More evidence beside MALDI-TOF mass spectra is required to clarify the exact chain end structures. Based on the MS and NMR observation the various chain end structures are postulated. Side reactions that lead to these chain ends are also postulated which mainly include β-proton elimination, water capping of the carbocationic chain end combinations of these reactions.

6.1.2 *Ab initio* chain end functionalisation via alkylation of silyl enol ethers

In this research silyl enol ethers were applied as end-capping agents and were added to cationic polymerisations of vinyl ethers before initiation. End-capping agents compete with monomer to cap the carbocationic chain end during the polymerisation. When the end-capping rates are comparable with chain propagation rates, the systems allow chain propagation to progress so that oligomer chains are still formed but other termination reactions are suppressed. At the same time end capping gives the oligomer chain designed chain end functionalities.

Various initiation systems, monomers, polymerisation temperatures and end-capping agents were applied in this research. Table 6-1 compares the end-capping reaction results from various initiations systems. All these binary initiation systems in table 6-1 support end-capping of silyl enol ethers and chain end functionalities are obtained. Generally silyl enol ether functionalised oligomers have lower molecular weights and broader molecular weight distributions than their control polymerisations without end-capping.

Three silyl enol ethers including trimethyl-(1-phenyl-vinyloxy)-silane, trimethyl-(1-4-methoxyphenyl-vinyloxy)-silane and 2,2-dimethyl-1-(methylene-propoxy)-trimethyl-silane were applied as end-capping agents in the iBVE-HCl/$Yb(OTf)_3$ initiation system and were successfully alkylated *in-situ* by the propagating carbocationic chain end. After the increase of the initial silyl enol ether concentrations apparently end-capping rates were increased to be comparable to chain propagation rate, so that high chain end functionalities were obtained and side reactions were largely reduced as observed from both MALDI-TOF MS and NMR analysis. However, the functionalised oligo(isobutyl vinyl ether)s have very broad molecular weight distributions as shown in table 6-1.

Table 6-1: Polymerisation and chain end functionality data of different initiation systems

Initiator	Co-initiator	Monomer	Temp. °C	SEE	M_n	PD	Fn[α] %	Conv. %
	$Yb(OTf)_3$	iBVE	-30	1	670	8.10	86.9	100
				2	1010	6.90	93.2	90 4
				3	1280	1.5	N/A	100
iBVE-HCl	$SnCl_4$	iBVE	-78	1	590	2.07	85.8	81.5
				2	850	2.85	64.6	100
				3	1380	1.31	N/A	100
				4	1210	2.20	N/A	100
				5	2360	1.31	0	41 9
		EVE	-78	1	740	2.75	92	100
		MVE[β]	-78	3	570	1.50	N/A	48.8
				4	1460	1.57	N/A	76.0
	$SnBr_4$	iBVE	-15	1	960	3.98	70.2	98.5
HCl	$ZnCl_2$	iBVE	-78	2	460	2.19	34.0	75.7

All polymerisations have the initial ratio of [M]:[Initiator]:[SEE]=10:1:1

[α]: Chain end functionality data were obtained from ^{1}H NMR analysis. This method is not applicable for **SEE 3** and **SEE 4** functionalised chain end.

[β]: *n*-Bu_4NCl was applied in the polymerisation of MVE

$HCl/ZnCl_2$ gave a better-defined cationic polymerisation of isobutyl vinyl ether at -78°C but the chain end functionalisation was not as successful as other initiation systems.

iBVE-HCl/$SnBr_4$ and iBVE-HCl/$SnCl_4$ give similar cationic polymerisation and chain end functionalisation results. Six silyl enol ethers were applied in cationic polymerisation of isobutyl vinyl ether in iBVE-HCl/$SnCl_4$ initiation system. Among the six silyl enol ethers, trimethyl-(1-phenyl-vinyloxy)-silane and [1-(4-methoxy-phenyl)-vinyloxy]-trimethyl-silane gave high chain end functionalities, (1-*tert*-butyl-vinyloxy)trimethyl-silane and (1-methoxy-2-methyl-propenyloxy)-trimethyl-silane gave medium to high chain end functionalities, and 3-methoxy-1-methylene-allyloxy)-trimethyl-silane and (cyclohex-1-enyloxy)-trimethyl-silane failed to attach to the carbocationic chain end. Even with high chain end functionalities the oligomers

obtained from this initiation system generally have much lower PD than functionalised oligomers obtained from iBVE-HCl/Yb(OTf)$_3$ initiation system.

It was observed that *ab initio* chain end functionalisation by reactive silyl enol ethers largely suppresses the majority of side reactions that occur during conventional polymerisation. This suppression was attributed to either the higher competition rates of end-cappings than side reaction rates, or the capping of the formed side reaction chain end— it is considered that reactive silyl enol ethers can even cap the aldehyde and diisobutanol chain ends formed during polymerisation and can increase the chain end functionality.

Ab initio end-capping of silyl enol ethers were proved also reactive in the cationic polymerisation of ethyl vinyl ether and methyl vinyl ether. Different silyl enol ether reactivities in end-capping were observed. Temperature was considered to affect the chain end functionality generally through its affect to side reactions. Low temperature reduces side reaction and thus enhances the end-capping and improves the chain end functionality, although variations are also observed.

When (1-*tert*-butyl-vinyloxy)trimethyl-silane was applied as end-capping agent, the polymerisation system produced oligomers with narrower PD than the control polymerisation without end-capping while the chain end high functionalities were also obtained. This indicates the possibility to set up a controlled *ab initio* chain end functionalisation cationic polymerisation system in which oligomer's M_n, PD and chain end functionality can be regulated at the same time.

6.1.3 Mass spectrometric analysis in *ab initio* chain end functionalisation

While NMR and IR sometimes offer the structure—dependent information on polymer samples, accurate compositional information can be obtained by the structure—independent mass spectra of synthetic polymers that can be used to analyse end groups and structures of polymer chains. With the good resolution of this technique, accurate polymer mass can be obtained to detect the different polymer chain end structures formed during polymerisation and thus the side reactions can be analysed. Application of MALDI-TOF mass spectrometry highly enhanced analysis in the current *ab initio* chain end functionalisation research.

Reproducible sample preparation is one of the crucial aspects in MALDI-TOF MS analysis. Oligomer concentration, various matrices, ionisation agents and their concentrations were investigated. For the analysis of oligo(vinyl ether)s, DHB instead

of dithranol at a relatively low concentration of 10 mg cm^{-3}, with the oligomer's concentration from10 mg cm^{-3} to 0.2 mg cm^{-3} was found to be the optimum matrix.

Direct laser desorption of oligo (isobutyl vinyl ether) was observed for the samples of molecular weight of up to 2k Daltons. Sodium ion was found to be attached to these oligomer chains from direct laser desorption. The sodium ionisation was considered to come from the recovery procedure after the polymerisation, and/or from contamination. Apart from sodium ionisation, potassium, proton, silver ionisations are also observed in the analysis.

Complementary information of oligo(isobutyl vinyl ether)s obtained from ESI MS indicates mass discrimination in MALDI-TOF technique and thus it is regarded that MALDI-TOF MS can not provide reliable molecular weight distribution for polymers with broad molecular weight distributions. Combination of SEC and MALDI-TOF MS offers a method to obtain accurate molecular weight parameters [Wu, 1998; Simonsick, 1993]. In this research a SEC fractionation followed by MALDI-TOF MS analysis was performed with oligo(isobutyl vinyl ether) and the average molecular weight of each SEC fraction was calculated. These data obtained can be used to calibrate SEC column and to calculate molecular weight and the molecular weight distribution of the oligomer sample.

MALDI-TOF mass spectra can be applied in analysing oligo(vinyl ether)s for chain end functionality information qualitatively and even quantitatively under limited conditions. It is generally regarded that quantitative analysis by MALDI-TOF MS is not reliable due to the uneven sample distribution, uneven polymer ion desorption and uneven ionisation procedure. However, the current research explored quantitative application of this technique in chain end functionality analysis. Chain end functionality data from MALDI-TOF mass spectra were shown to be in accordance with ^{1}H NMR analysis. This proved that under limited conditions this technique could be applied quantitatively. However, it must be taken into consideration that because of the underpresentation of polymers with higher mass, the use of the intensity of polymer ions may not be a very precise method of calculating chain end functionalities of the polymer samples. Nonetheless, when other measurement techniques are not available MALDI-TOF MS can be used for the estimation of chain end functionality and the method has the advantage that many samples can be analysed in a short period.

6.2 Consideration on the future work

As introduced in chapter 1 the new techniques in the development of macromolecular engineering will be applied in the well-defined materials preparation [Kennedy, 1998]. Future research on *ab initio* chain end functionalisation should also focus on the well-defined material preparation, i.e., to obtain a controlled polymerisation in which molecular weight, polydispersity and chain end functionality are regulated at the same time.

6.2.1 Kinetic research

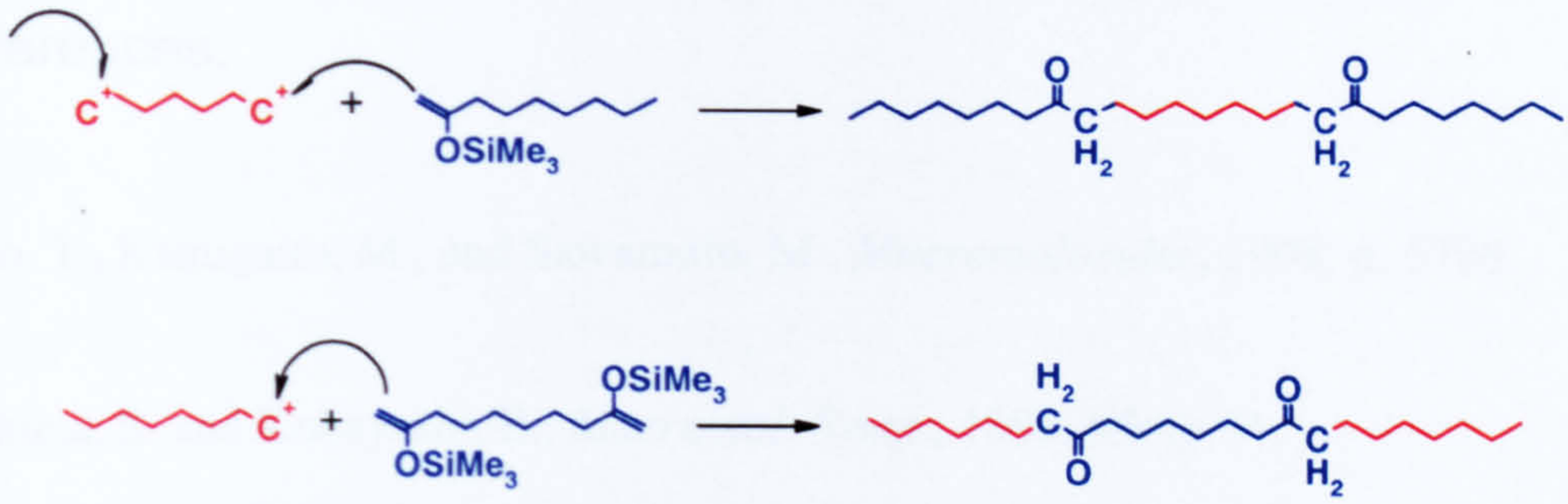
Kinetic research is required to obtain the end-capping reaction rate constant and chain propagation rate constant. *ab initio* chain end functionalisation offers an alternative way of end-capping of living chain ends. Side reactions are possible in the reaction system but they can be suppressed. Thus *ab initio* chain end functionalisation requires a comparable end-capping rate and chain- propagation rate so that chain propagation can progress while side reactions are suppressed. Also initial concentrations of end-capping agents are not assumed to be low to overcome the possible fast side reactions if there is any.

In the current research the kinetic data of chain propagation and end-capping reactions are not available, so that only relative concentrations of monomer and end-capping agents are regulated to adjust the relative reaction rates. To achieve delicate control over the polymerisation and end-capping, kinetic data on chain propagation reaction, end-capping reaction and side reactions need to be obtained.

6.2.2 Preparation of block-copolymer

Ab initio chain end functionalisation using a difunctional initiator can produce telechelic silyl enol ether functionalised oligomer chains. Further reactions can give ABA type block-copolymer.

Also as shown in scheme 6-1 difunctional silyl enol ether can be applied in cationic polymerisation to give the polymer chain with silyl enol ether functionality. The silyl enol ether functionality can be again applied to cap the carbocationic chain end and produce a block-copolymer.



Scheme 6-1: Synthesis of block copolymer using silyl enol ether functionalisation

6.2.3 *Ab initio* chain end functionalisation in aqueous cationic polymerisation

Environmentally benign aqueous cationic polymerisation has been proved to be possible [Satoh, 2000]. The water stable Lewis acid catalysed aqueous aldol reaction was also feasible [Kobayashi, 1994; Hachiya, 1994; Kobayashi, 1998]. The Lewis base catalysed aldol reaction of dimethylsilyl enolates with benzaldehyde in aqueous dimethylformamide gives high yield [Miura, 2002] and this proved the relative stability of the silyl enolate in aqueous solution. The *ab initio* chain end functionalisation in aqueous cationic polymerisation is thus possible and deserve to be tried.

6.2.3 Quantitative analysis on chain end functionality using MALDI-TOF MS

More research needs to be carried out on investigating the possibility of quantitative analysis of MALDI-TOF MS on the chain end functionality. The current research found that various chain ends did not affect the sodium ionisation and that within a narrow mass range the relative intensities of oligomers with different chain ends can be compared. However, due to the mass discrimination, data on the average chain end functionality might be in error. When other techniques are not available and the mass discrimination can be neglected the chain end functionality of the oligomer sample can be obtained from MALDI-TOF MS.

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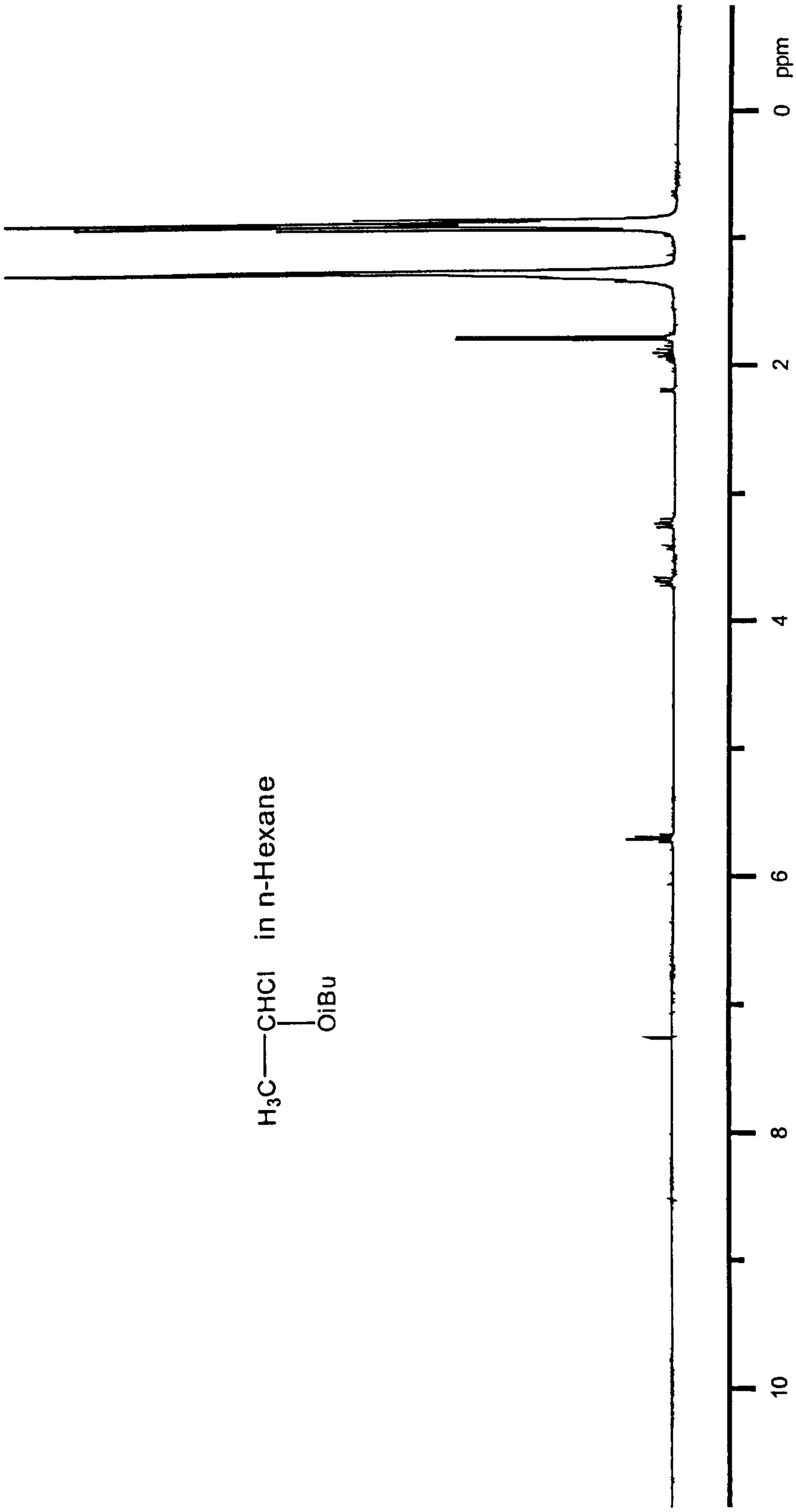
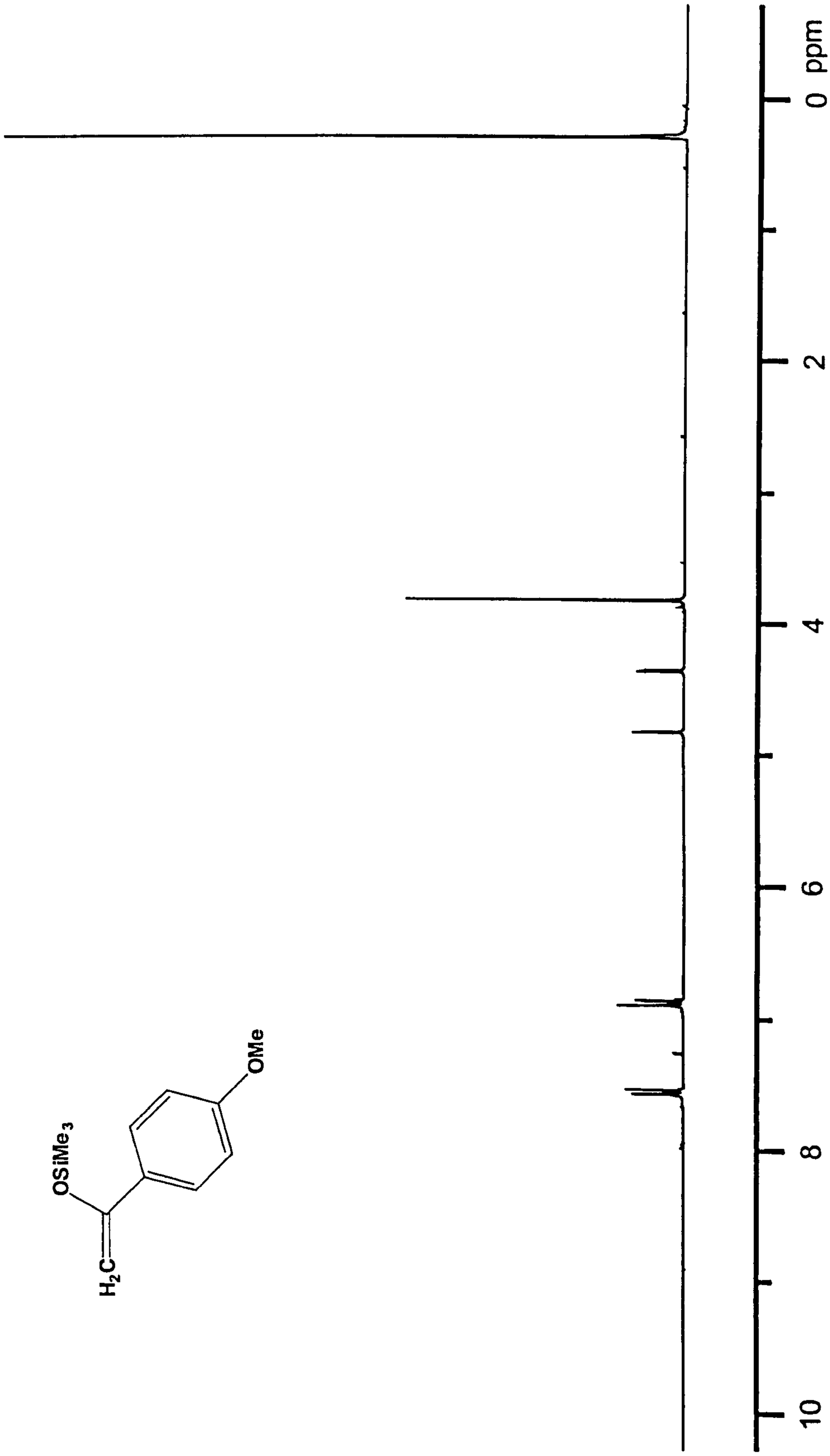
Appendix A. Spectra of the Small Molecules Synthesised

List of the spectra:

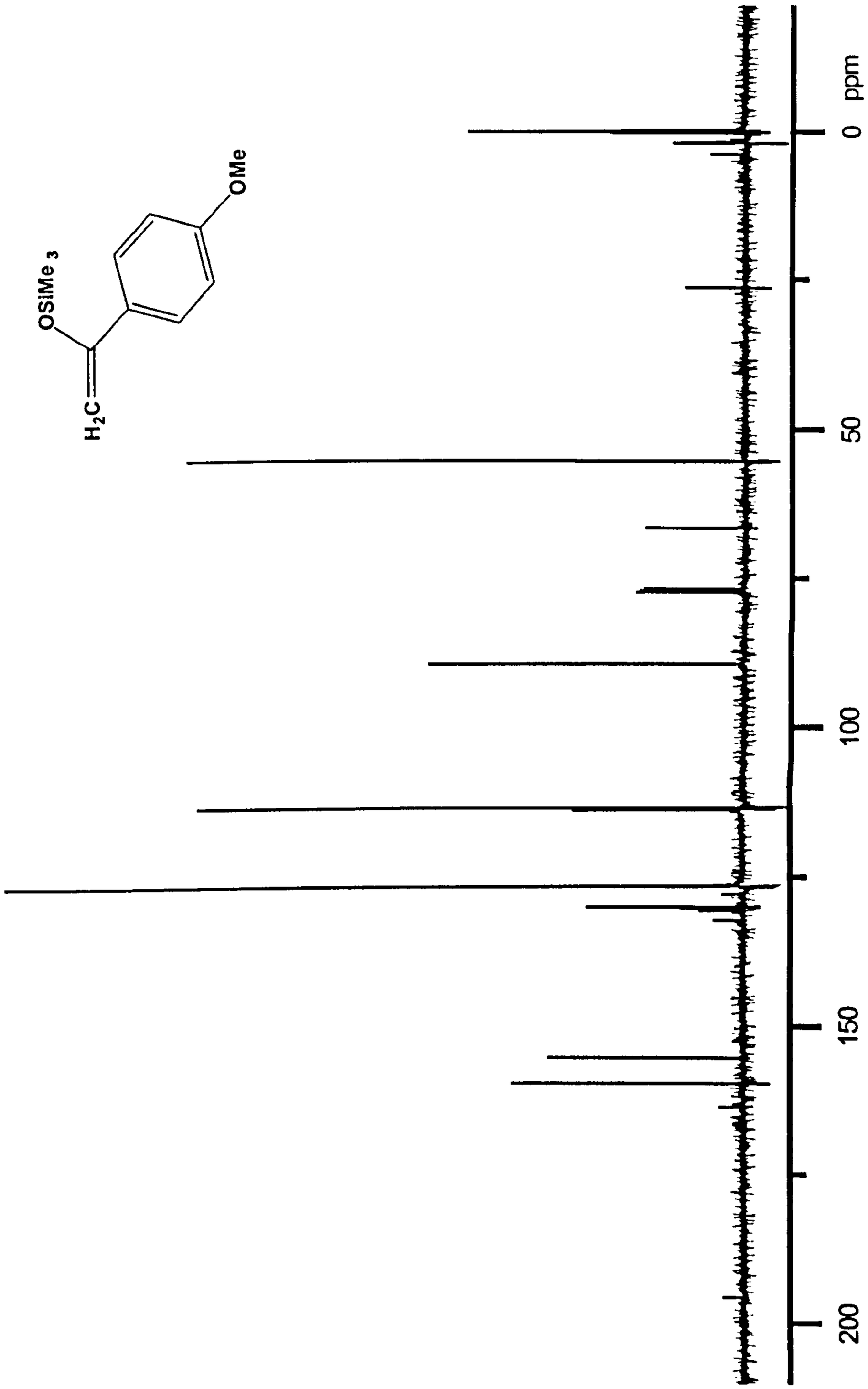
1. ^{1}H NMR spectrum of 1-(1-Chloro-ethoxy)-2-methyl-propane in *n*-Hexane
2. ^{1}H NMR spectrum of Trimethyl-(1-4-methoxyphenyl-vinyloxy)-silane
3. ^{13}C NMR spectrum of Trimethyl-(1-4-methoxyphenyl-vinyloxy)-silane
4. Mass spectrum of Trimethyl-(1-4-methoxyphenyl-vinyloxy)-silane
5. ^{1}H NMR spectrum of 2,2-Dimethyl-1-(methylene-propoxy)-trimethyl-silane
6. ^{13}C NMR spectrum of 2,2-Dimethyl-1-(methylene-propoxy)-trimethyl-silane
7. Mass spectrum of 2,2-Dimethyl-1-(methylene-propoxy)-trimethyl-silane



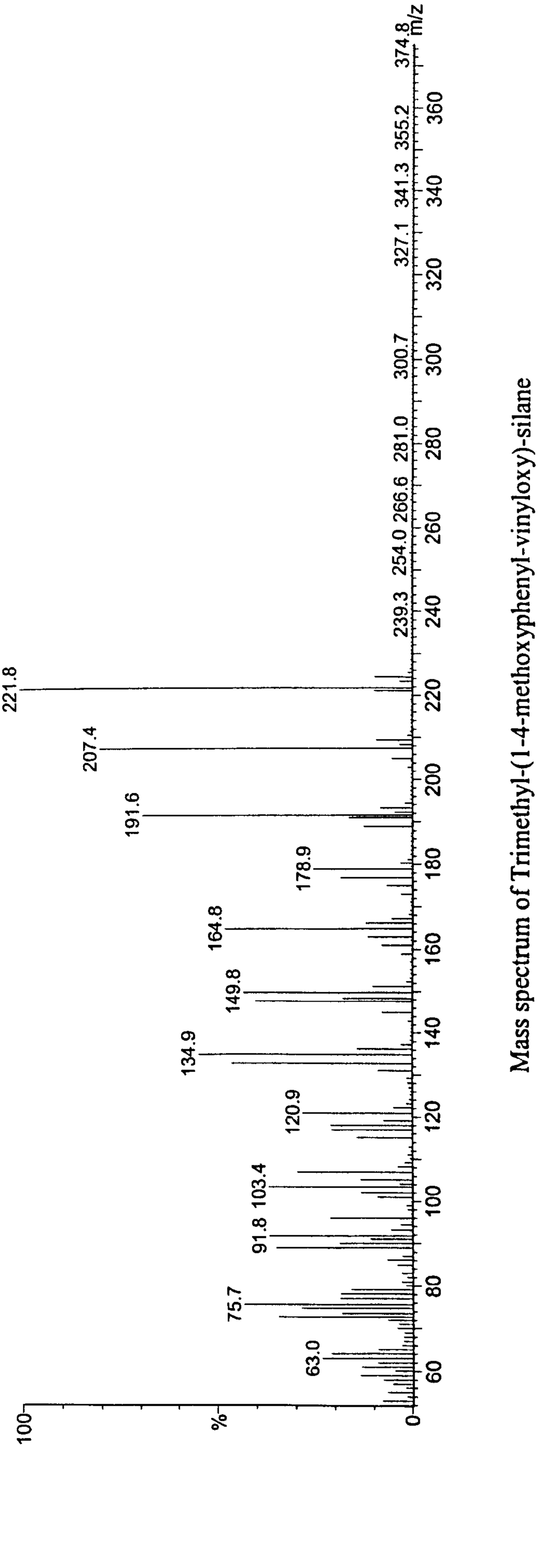
^{1}H NMR spectrum of 1-(1-Chloro-ethoxy)-2-methyl-propane in *n*-Hexane



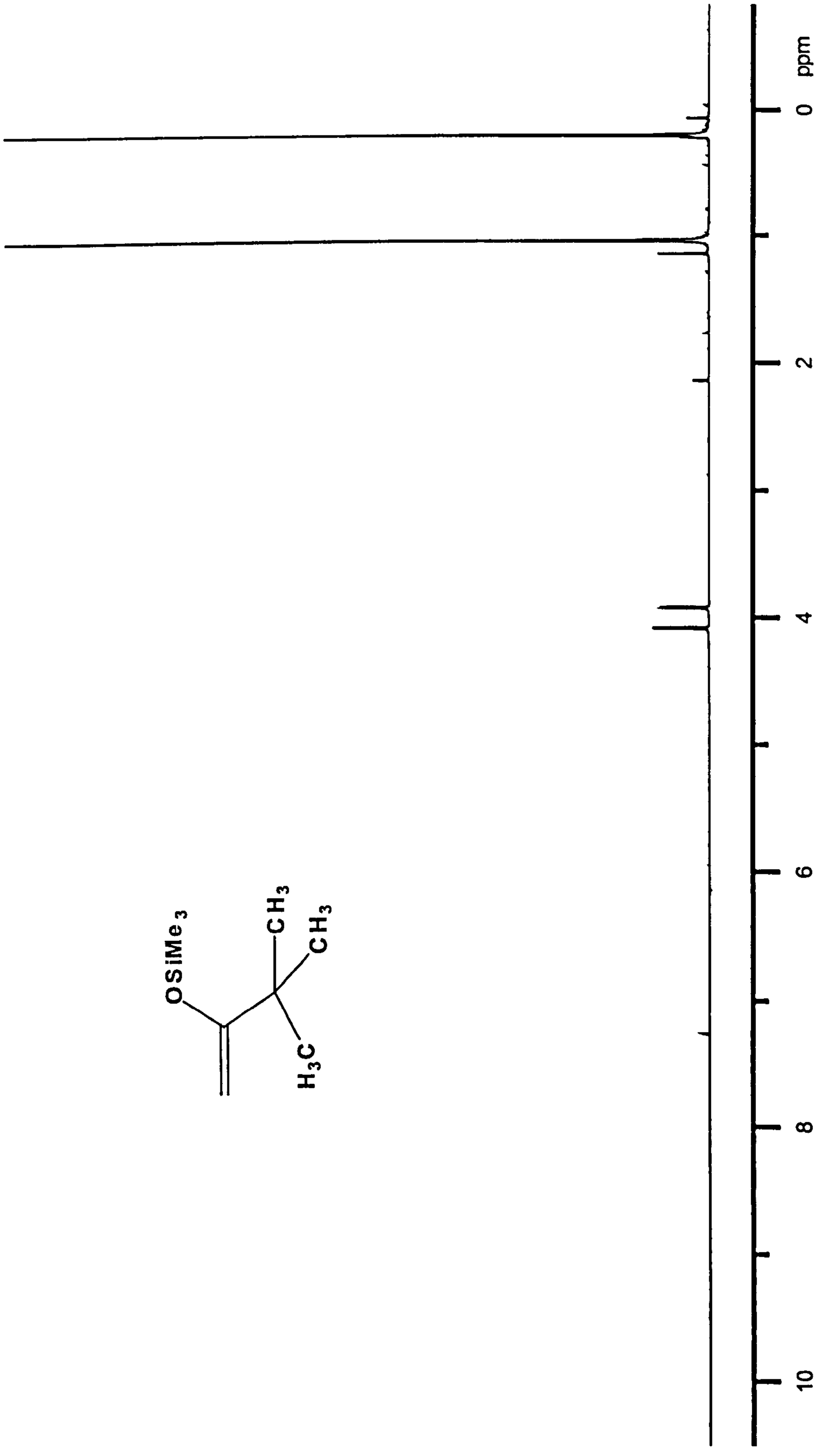
^{1}H NMR spectrum of Trimethyl-(1-4-methoxyphenyl-vinyloxy)-silane



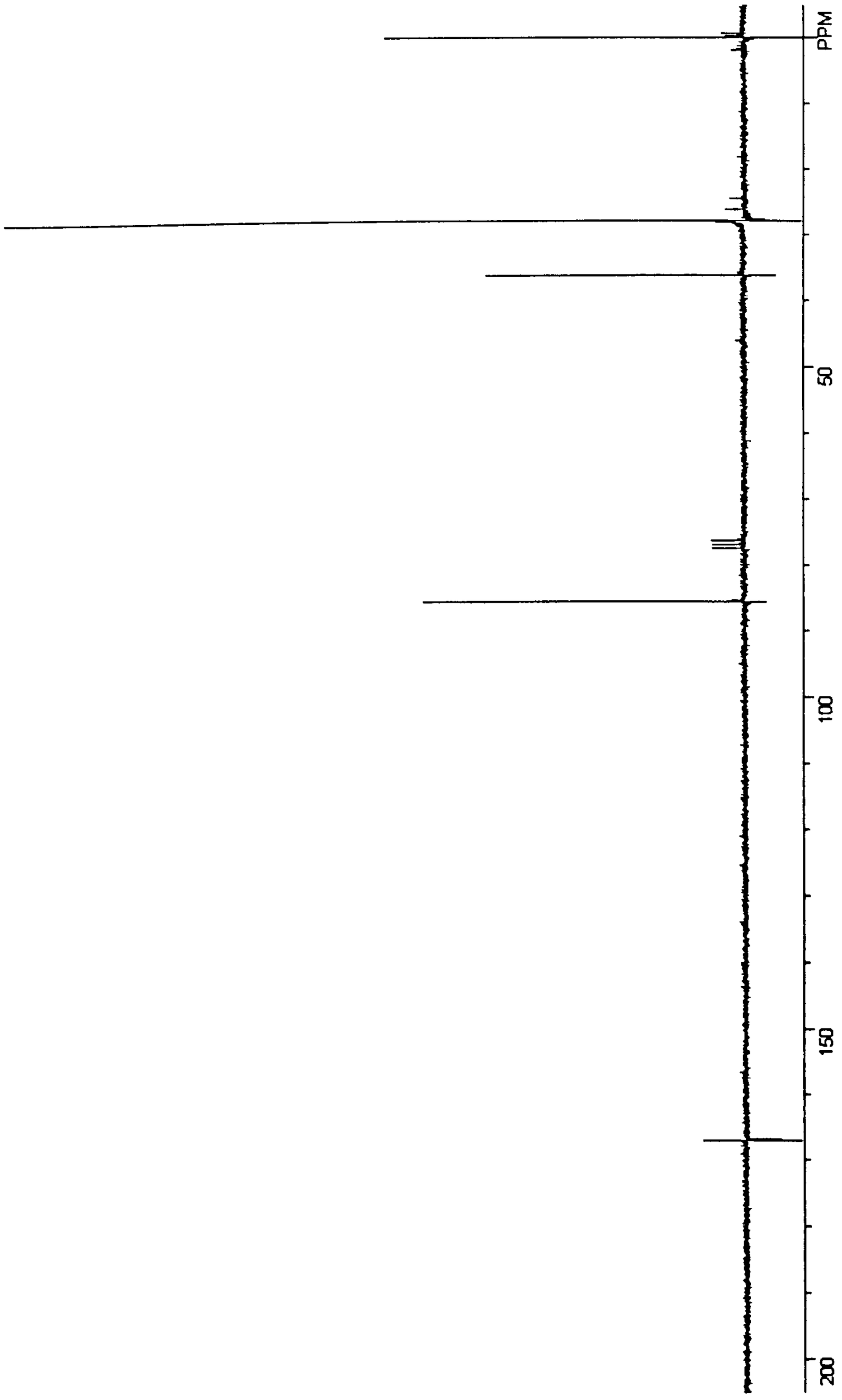
^{13}C NMR spectrum of Trimethyl-(1-4-methoxyphenyl-vinyloxy)-silane



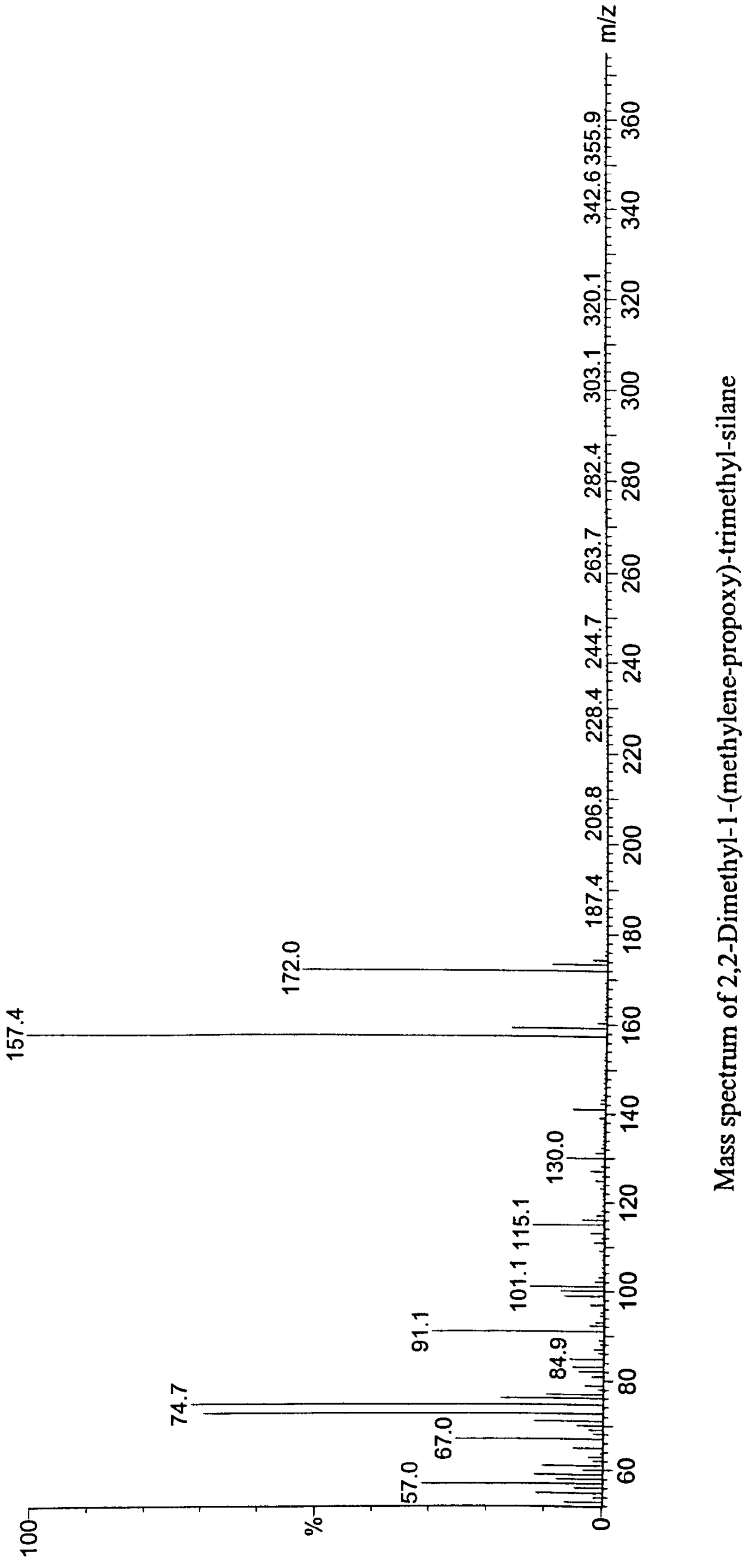
Mass spectrum of Trimethyl-(1-4-methoxyphenyl-vinyloxy)-silane



^{1}H NMR spectrum of 2,2-Dimethyl-1-(methylene-propoxy)-trimethyl-silane



^{13}C NMR spectrum of 2,2-Dimethyl-1-(methylene-propoxy)-trimethyl-silane



Mass spectrum of 2,2-Dimethyl-1-(methylene-propoxy)-trimethyl-silane

Appendix B. Publications arising from the research

1. Weihong Lang, Steve Rimmer, "*Synthesis of Telechelic Oligo(isobutyl Vinyl Ether)s via Alkylation of Silyl Enol Ethers by Propagating Chain End by an ab Initio Cationic Polymerisation*", *Macromolecular Rapid Communications*, Vol. 22, Feb 2001 pp194-198, (Front Cover)

2. Weihong Lang, Steve Rimmer, "*Mass Spectrometric Analysis of Chain End Functionalization in ab initio Cationic Polymerisation*", *Macromolecular Symposia*, Volume 184, Issue 1, 2002, pp311-324

3. Steve Rimmer, Weihong Lang, Prodip Sarker, "*ab initio Cationic Polymerisation of Vinyl Ethers*", *Polymer Preprints (Am. Chem. Soc., Div. Polym. Chem.)*, 2002, 43(2), pp971

4. Weihong Lang, Prodip Sarkar, Steve Rimmer, "*ab initio Chain End Functionalization via Alkylation of Silyl Enol Ethers in Cationic Polymerisation of Vinyl Ethers*", in preparation for *Chemistry*

5. Weihong Lang, Prodip Sarkar, Steve Rimmer, "*ab initio Chain End Functionalization via Alkylation of Silyl Enol Ethers in Cationic Polymerisation of Vinyl Ethers*", in preparation for *Macromolecules*

6. Weihong Lang, Zuifang Liu, Steve Rimmer, "*Application of MALDI-TOF MS on Various Polymer and Polymerisation Process Analysis*", in preparation